# Mechanisms of Isomerization of Hydrocarbons on Metals

Part 11.—Isomerization and Dehydrocyclization of <sup>13</sup>C-labelled 3-Methylhexanes on Pt-Al<sub>2</sub>O<sub>3</sub> Catalysts

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The isomerization, dehydrocyclization and hydrogenolysis of 3-methylhexane have been studied at 320-380°C over a series of Pt-Al<sub>2</sub>O<sub>3</sub> catalysts with a metal dispersion extending from 0.05 to 1. The use of five labelled compounds, 3-methyl[1-1<sup>3</sup>C], [2-1<sup>3</sup>C], [3-1<sup>3</sup>C], [6-1<sup>3</sup>C]hexanes and 3-methyl-[1<sup>3</sup>C]hexane, allowed distinction between the various parallel pathways.

On all catalysts the predominant reaction was the isomerization according to a cyclic mechanism involving either 1,3-dimethyl-, 1,2-dimethyl- or ethyl-cyclopentane intermediates with a relative contribution of 60, 40 and 20 %, respectively. These results are consistent with a dehydrocyclization scheme involving a metallocarbene as precursor and dicarbene or dicarbyne recombination as the rate-determining step.

In the preceding papers,<sup>1</sup> it has been shown that the reaction mechanisms involved in heptane isomerizations, cyclic and bond-shift, are basically the same as those involved in the rearrangement of smaller molecules. The demonstration was only possible because for the molecules investigated, 2,3-dimethylpentane and 2-methylhexane, the occurrence of a single dehydrocyclization path minimizes to some extent the number of reaction products. In this paper a more complex molecule, 3-methylhexane, has been selected for more detailed study of the various reaction mechanisms.

Three dehydrocyclization pathways involving 1,2-dimethyl-,1,3-dimethyl- and ethyl-cyclopentane intermediates and twelve bond-shift reactions including four alkyl displacements and four chain shortenings are possible for this molecule, yielding a complete spectrum of all  $C_7$  hydrocarbons, most of which are obtained by different routes (fig. 1). Owing to this complexity, it is not possible using a single labelled molecule to distinguish between the different paths: five labelled molecules have therefore been used (table 1). Moreover, since chain shortening or chain lengthening by bond-shift, and reactions yielding molecules with quaternary carbon atoms have been shown to have a minor part in heptane isomerizations, the main emphasis has been laid upon the distinction between dehydrocyclization pathways (1)-(9) and alkyl displacement reactions (10)-(12).

### EXPERIMENTAL

### GAS CHROMATOGRAPHY

A 5 m long  $\frac{1}{8}$  in DC 200 column operating at 30°C was systematically used to analyse a small fraction of the reaction products after hydrogenation. On this column 2,3-dimethylpentane and 2-methylhexane were only partly resolved and 1,2-*trans*-, 1,3-*cis*- and 1,3-*trans*dimethylcyclopentanes and ethylpentane were eluted in a single broad chromatographic peak. In some complementary analyses, better resolution of 2-MH and 2,3-DMP was achieved on a 5 m by  $\frac{1}{8}$  in column of 6% squalane on firebrick at 40°C<sup>8</sup> and partial separation was achieved on a 5 m DMS column operating at 0°C of the three dimethylcyclopentanes Published on 01 January 1980. Downloaded by Cornell University Library on 19/07/2016 23:19:03.





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TABLE 1(a)         LABELLED	<b>n-heptanes</b>	AND	2-METHYLHEXANES	EXPECTED	IN	3-METHYLHEXANE
		ISO	MERIZATION			

products		n-heptane				
mechanisms	bo	nd-shift	cyclic	mechanism		
reactants	(C)	(C')	(1,2-DMCP)	(EtCP)		
(I-X)	$3^{-13}C(z)$	$4^{-13}C(t)$	$1^{-13}C(x)$	$\begin{cases} 1^{-13}C(x) \\ +4^{-13}C(t) \end{cases}$		
(I-Y)	$2^{-13}C(y)$	$2^{-13}C(y)$	$2^{-13}C(y)$	$2^{-13}C(y)$		
• (I-Z)	$1^{-13}C(x)$	$1^{-13}C(x)$	$1^{-13}C(x)$	$1^{-13}C(x)$		
(I-W)	$1^{-13}C(x)$	$1^{-13}C(x)$	$3^{-13}C(z)$	$\begin{cases} 2^{-13}C(y) \\ + 3^{-13}C(z) \end{cases}$		
(I-T)	$4^{-13}C(t)$	$3^{-13}C(z)$	$2^{-13}C(y)$	$3^{-13}C(z)$		
produc	cts	2-methylhexane				
mechanis	sms	bond-shift	cyclic meel	hanism		
reactar	nts	(MeSh)	(1,3-DM	CP)		
$\sim$	(I–X)	$1-^{13}C(x')$	$1^{-13}C(x') + 6$	$5^{-13}C(z')$		
$\sim$	(I-Y)	$2^{-13}C(y')$	$3^{-13}C(u') + 4$	$-^{13}C(v')$		
$\sim$	(I–Z)	$1^{-13}C(x')$	$3^{-13}C(u') + 4$	$-^{13}C(v')$		
$\sim$	(I-W)	6- <sup>13</sup> C(z')	$1^{-13}(Cx') + 6$	$5^{-13}C(z')$		
$\sim$	(I–T)	$3^{-13}C(u')$	$2^{-13}C(y') + 5$	$5^{-13}C(w')$		

## (b) Self-isomerized 3-methylhexanes

products		3-methylhexane								
mechanisms	bon	d-shift	cyclic mechanisms							
reactants	(MeSh)	(PrSh)	(1,2-DMCP)	(1,3-DMCP)	(EtCP)					
(I-X) (I-Y) (I-Z) (I-W) (I-T)	$\begin{array}{c} \text{Me-}^{13}\text{C}(x'') \\ 5^{-13}\text{C}(v'') \\ 6^{-13}\text{C}(w'') \\ 1^{-13}\text{C}(z'') \\ 4^{-13}\text{C}(u'') \end{array}$	1- <sup>13</sup> C(z") 3- <sup>13</sup> C(t") Me- <sup>13</sup> C(x") 6- <sup>13</sup> C(w") 2- <sup>13</sup> C(y")	$1^{-13}C(z'')$ $3^{-13}C(t'')$ Me <sup>-13</sup> C(x'') $4^{-13}C(u'')$ $2^{-13}C(y'')$	6- <sup>13</sup> C(w") 1- <sup>13</sup> C(z") 2- <sup>13</sup> C(y") Me- <sup>13</sup> C(x") 5- <sup>13</sup> C(v")	4- <sup>13</sup> C(u") 2- <sup>13</sup> C(y") 1- <sup>13</sup> C(z") 5- <sup>13</sup> C(v") 3- <sup>13</sup> C(t")					

and ethylpentane.<sup>2</sup> Before mass spectrometric analysis the reaction mixture was separated into three fractions on a 5 m by  $\frac{1}{4}$  in 20 % SE 30 column at 20°C, each fraction was then hydrogenated on Pt-Al<sub>2</sub>O<sub>3</sub>. These fractions included : (1) all the cracking products and most of the 3-methylhexane, (2) all the saturated acyclic isomers, olefins and cyclopentane molecules and (3) toluene.

#### MASS SPECTROMETRY

The treatment of mass spectra has already been described.<sup>1</sup> 2,3-DMP and 2-MH were only partly resolved, even at  $-20^{\circ}$ C on the DC 200 chromatographic column used in the g.l.c.-m.s. device. However, because of the high sensitivity of  $(C_6H_{13})^+$  ions in the mass spectrum of 2-MH (10 times that of the corresponding ions obtained from 2,3-DMP), it was possible to determine accurately the mole fractions of the heavy and light hexyl ions obtained from 2-methylhexane.

#### CATALYSTS

Six  $Pt-Al_2O_3$  catalysts, with mean metal particle sizes ranging from 10 to 200 Å, were prepared by impregnation of a catalytically inert alumina (Woelm A.G) with chloroplatinic acid. The continuous change in metal dispersion, a, as defined by the ratio between the superficial and total platinum atoms, was obtained (1) by changing the metal content of the catalyst from 0.2 to 10 % and (2) by modifying by calcination at 600°C the dehydroxylation state of alumina.<sup>3</sup> The catalyst with a nominal metal loading of m% on an alumina calcined for n h at 600°C is referred to as m % Bn, the 10 % Pt-Al<sub>2</sub>O<sub>3</sub> catalyst prepared with a non-calcinated alumina as 10 % A. Characterization of these catalysts by hydrogen chemisorption, X-ray diffraction, small-angle X-ray scattering and electron microscopy has been described elsewhere.<sup>4</sup> The H/Pt ratios, determined by hydrogen chemisorption, the characteristics of the E.M. histograms [extent (modes) and maxima] and the actual Pt and Cl contents obtained by X-ray fluorescence are reported below. The particle size distributions were monomodal in all catalysts except 10 % B 210 for which a secondary maximum was found in the histogram, at 55 Å.

catalysts	10 % A	10 % B 10	10 % B 210	4 % B 210	2 % B 210	0.2 % B 210
a = H/Pt E.M. histograms modes	0.05	0.12	0.35 (10-35) (50-70)	0.55 (5-30)	0.70 (5-25)	1.0 (5-35)
maxim. Pt % Cl %	90 <sup>a</sup> 10 0.5	70 <sup>a</sup> 8.4 0.6	22 7.1 0.76	18 4.1 0.6	12 2.5 0.6	10 0.25 0.22

<sup>a</sup> Mean particle size determined by X-ray line broadening.

Because of the high reaction temperature, 320-380°C, the possible bifunctionality of the Pt-Al<sub>2</sub>O<sub>3</sub> catalysts was checked as follows. 3-methylhexene was reacted on pure alumina under the same conditions that were used for 3-methylhexane isomerization on  $Pt-Al_2O_3$ . Less than 1 % olefin reacted, in comparison with 35 % 3-methylhexane, and yielded mainly cracking products. To eliminate any possible effect of chlorine, Pt-Al<sub>2</sub>O<sub>3</sub> catalysts with chlorine contents of 0.2 and 1.2 % were compared and no alteration was observed either in the rates or in product distributions.

### RESULTS

#### PRODUCT DISTRIBUTIONS

### **ISOMERIZATION AND DEHYDROCYCLIZATION**

Reactions of 3-methylhexane (3-MH:5 Torr) have been studied at 320-380°C under atmospheric hydrogen pressure and on Pt-Al<sub>2</sub>O<sub>3</sub> catalytss with various

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dispersions. On all catalysts, C<sub>7</sub> hydrocarbons initially represented 80-85 % of the reaction products and included mostly 2,4- and 2,3-dimethylpentanes (2,4-DMP, 2,3-DMP), 2-methylhexane (2-MH), n-heptane (n-Hep), 1,2- and 1,3-dimethylcyclopentanes (DMCP), ethylcyclopentane (EtCP) and toluene (Tol). Small amounts of olefin were also present and increased with temperature. Their amounts corresponded roughly to those expected at equilibrium and they were hydrogenated in order to obtain the distribution of isomers classified according to their carbon skeleton (table 2). Ethylpentane could be estimated only to roughly  $3\pm 1$  % of the C<sub>7</sub> reaction products. Methylcyclohexane, resulting from hydrogenation of part of the toluene, was also present and amounted to < 2 %.

TABLE 2.—ISOMERIZATION OF	3-methylhexane.	DISTRIBUTION OF	C7	REACTION	PRODUCTS
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catalysts	H/Pt	T/°C	ατ	2,4-DMP	2,3-DMP <sup>c</sup> +2MH	DMCPa +EtP	n-Hep	MCH <sup>b</sup>	EtCP	Tol
10 % B 10	0.12	340	ID	6	18	53	10	2	11	
10 % B 210	0.35	360	ID	7	19	52	9	3	10	
0.2 % B 210	1.0	360	ID	7	18	53	9	3	10	
10 % B 10	0.12	340	14.9	8.0	25.2	40.8	11.0	2.1	6.4	6.5
10 % B 210	0.35	360	16.0	8.1	20.1	44.0	10.6	2.5	5.7	9.0
4 % B 210	0.55	360	17.4	8.1	22.8	41.5	12.4	2.5	5.4	7.3
2 % B 210	0.70	360	11.9	7.6	20.5	43.3	11.9	2.8	5.7	8.2
0.2 % B 210	1.0	360	16.1	9.0	21.4	44.8	10.7	2.5	5.3	6.3
10 % K	0.03	350	ID	0	30	34	11	2	13	
10 % B 10 <sup>d</sup>	0.12	340	15.2	9	26.5	43.5	12	2	7	
2 % B 210e	0.70	360	19.6	8.9	23.3	45.7	13.2	2.9	6.0	—

ID: Initial distribution, H/Pt: metal accessibility,  $\alpha_{\rm T}$ : total conversion (percents in weight of 3-methyl hexane having reacted). *a trans*- and *cis*-1,3-dimethylcyclopentanes + *trans*-1,2-dimethylcyclopentane (ratio 1.3:1); *b* methylcyclohexane + *cis*-1,2-dimethylcyclopentane; *c* 2,3-DMP/2-MH =  $\frac{1}{2}$ ; *d* run 1; *e* run 5.

With increasing conversion, the selectivity rapidly decreased : at total conversion  $\alpha_{\rm T}$  of 20 and 75 %, the percentages of hydrocracking products were 25 and 40, respectively, instead of the initial 15. Simultaneously the percentages of toluene in  $C_7$  hydrocarbons sharply increased from 4 % initially to 13 and 40 %. However, these toluene percentages fluctuated; therefore the percentages of non-aromatic C7 hydrocarbons were plotted against conversion in fig. 2 and 3 for two catalysts, 10 % B 10 and 10 % B 210, of low and medium metallic dispersion. With increasing conversion, the percentages of acyclic molecules increased at the expense of dimethyl- and ethyl-cyclopentanes. Extrapolation of the curves to zero conversion gives the initial distributions reported in table 2. These seemed to be independent of the metal dispersion, as confirmed by the product distributions obtained at 15 % conversion and reported in the second part of table 2. The cyclic molecules represented 65 %of the products and among them dimethylcyclopentanes predominated. A rough estimate of the ratio 1,3-DMCP/1,2-DMCP, made by analysis on a DMS column, gave a value of 1.3. Analysis on a squalane column gave a 2,3-DMP/2-MH ratio of 1:2.



FIG. 2.—Product distributions as a function of conversion  $\alpha_T$ , 10% B 10 at 340°C.  $\blacklozenge$ , 2-MH+2,3-DMP;  $\diamondsuit$ , 1,2-DMCP trans;  $\Box$ , EtCP;  $\blacksquare$ , 2,4-DMP;  $\checkmark$ , n-Hep.

Increasing the temperature from 340 to  $385^{\circ}$ C increased by 50 % the amount of toluene formed initially and also increased to a smaller extent (10%) the percentage of cyclic molecules.

### HYDROCRACKING

The distributions of hydrocracking products were independent of temperature and metal dispersion, neither did they depend on conversion, up to 60 %. Since there was never intensive cracking to methane or consecutive cleavage of several C—C bonds, hydrogenolysis must take place according to one of the following reactions:

demethylation (51+4%):  $C_7 \rightarrow C_6 + C_1$  (22)

de-ethylation 
$$(25 \pm 4 \%)$$
 :  $C_7 \rightarrow C_5 + C_2$  (23)

depropylation 
$$(24 \pm 4 \%)$$
:  $C_7 \rightarrow C_4 + C_3$ . (24)

A detailed analysis of the cracking products (fig. 4) shows a distribution not far from that provided by statistical cleavage of any C—C bond. However, depropylation and demethylation producing 2-methylpentane predominate. Apart from acyclic hydrocracking products, methylcyclopentane (15% C<sub>4</sub>-C<sub>6</sub> hydrocarbons) and, in some experiments benzene, (< 3 %) were also formed, probably by consecutive demethylation of dimethylcyclopentanes and toluene.

### ABNORMAL CATALYST

In order to investigate possible effects of pretreatment,  $Pt-Al_2O_3$  10 % B 10 was heated in oxygen at 770°C for 12 h and reactivated in hydrogen at 300°C for 24 h.

The resulting catalyst, 10 K, behaved abnormally in both isomerization and hydrogenolysis reactions. The initial distribution of non-aromatic  $C_7$  hydrocarbons is reported in table 2. When compared with normal catalysts, 10 K yields smaller amounts of DMCP and practically no 2,4-DMP. The cracking pattern was also



FIG. 3.—Product distributions as a function of conversion  $\alpha_T$ , 10% B 210 at 360°C.  $\bigtriangledown$ , n-Hep;  $\blacksquare$ , 2,4-DMP;  $\Box$ , EtCP.



FIG. 4.-Hydrocracking of 3-methylhexane.

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different from that obtained on normal catalysts (fig. 5). The large amounts of isobutane formed (16 % of hydrogenolysis products) show the occurrence of consecutive cleavage of two carbon-carbon bonds. Such consecutive reactions in the adsorbed phase could also account for the amounts of n-butane and pentanes which are larger with respect to hexanes in catalyst 10 K than in the normal catalysts.



FIG. 5.-Hydrocracking on normal catalysts.

## **ISOMERIZATION OF LABELLED 3-METHYLHEXANES**

Isomerization of 3-methylhexanes labelled on carbons 1, 2, 3 and 6 and on the methyl group was effected at 360°C under atmospheric hydrogen pressure and on Pt-Al<sub>2</sub>O<sub>3</sub> catalysts of various dispersions. In each run, the carbon-13 was located in n-heptane, 2-methylhexane and 3-methylhexane.

#### **n-heptane**

In principle, the concentrations x, y, z and t of all four n-heptanes  $[1^{-13}C](X)$ ,  $[2^{-13}C](Y)$ ,  $[3^{-13}C](Z)$  and  $[4^{-13}C](T)$  may be calculated from eqn (1)-(4)

$$\sum_{x} x a_{nx} = a_{n} \qquad n = 6, 5, 4 \tag{1)-(3)}$$

$$\sum_{x} x = 1. \tag{4}$$

However, because  $(C_6H_{13})^+$  ions were small and  $-CH_3$  fragmentation was not unequivocal, determination of  $a_6$  was inaccurate and only three equations [(2)-(4)] involving  $a_5$  and  $a_4$  were used. Since, at most, three isotopic varieties were present in the n-heptanes mixture according to fig. 1 and table 1, these equations are sufficient for calculation of z, t and x or x + y (table 3).  $a_6$  was then recalculated using eqn (1) and compared with the observed values : the agreement was good.

Isomerization of 3-methyl-[1-13C]hexane (I-Z) and -[2-13C]hexane (I-Y) should yield only a single labelled heptane, (X) and (Y), respectively. Indeed, the amount of (Z) was not significant (accuracy  $\pm 3$  %) but tiny amounts of (T) were formed, showing the occurrence to a small extent of repetitive processes or additional mechanisms.

The isomerization of 3-methyl[<sup>13</sup>C]hexane (I-X) yields (Z) by propyl shift (C) and (T) by both ethyl shift (C') and the cyclic mechanism (EtCP), via an ethylcyclopentane intermediate (table 1). In table 3, a tendency for z to decrease and t to increase with increasing metal dispersion (H/Pt) is noticeable. Assuming bond-shifts (C) and (C') are equivalent, the contributions of the four possible reaction mechanisms were estimated from n-heptane concentration (table 4). With increasing metal dispersion the cyclic mechanism involving a DMCP intermediate decreased and that involving EtCP increased.

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TABLE 3.—ISOMERIZATION TO n-HEPTANE AT 360°C. DISTRIBUTION OF ISOTOPIC VARIETIES.

run	catalysts	H/Pt	$\alpha_{T}$		products		$\Delta a_6$
	thyl[ <sup>13</sup> C]hexane (1	[-X)					
				(x)	(z)	(t)	
1	10 % B 10 <sup>a</sup>	0.12	15.2	70	7.5	22.5	+0.03
2	10 % A <sup>a</sup>	0.05	28.4	72.5	5	22.5	-0.02
3	10 % B 210	0.35	16.8	68.5	7	24.5	-0.015
4	4 % B 210	0.55	17.4	71.5	6	23.5	+0.005
5	2 % B 210	0.70	19.6	71	3	26	+0.02
6	0.2 % B 210	1.0	1 <b>4.9</b>	67.5	5	27.5	+0.02
7	10 % K <sup>b</sup>	0.03	24.6	52.5	7.5	40	+0.03
3-me	thyl[1- <sup>13</sup> C]hexane	: (IZ)					
8	10 % B 210	0.35	21.9	97.5	-1.5	4.0	-0.04
9	2 % B 210	0.70	14.7	93	0.5	6.5	-0.01
3-me	thyl[2- <sup>13</sup> C]hexane	e (I-Y)					
				( <i>y</i> )	(z)	(t)	
10	10 % B 210	0.35	5.5	99.5	-4	4.5	+0.02
3-me	thyl[3-13Clhexane	(I-T)					
11	10 % B 210	0.35	16.0	50.5	48	1.5	-0.06
3-me	thvl[6- <sup>13</sup> C]hexane	e (I–W)					
				(x+y)	(z)	( <i>t</i> )	
12	10 % B 210	0.35	14.8	28.5	67	4.5	+0.01
13	10 % K <sup>b</sup>	0.03	30.6	53	44.5	2.5	-0.07

<sup>*a*</sup> Run made at 340°C, <sup>*b*</sup> at 380°C.

TABLE 4.—ISOMERIZATION OF 3-Me[<sup>13</sup>C]HEXANE TO n-HEPTANE. REACTION MECHANISMS.

run	catalysts	H/Pt	(C)	(C′)	(EtCP)	(DMCP)	(DMCP)/ (EtCP)
1	10 % B 10	0.12	7.5	7.5	30	55	1.85
3	10 % B 210	0.35	7	7	35	51	1.45
12 <sup>a</sup>	10 % B 210	0.35	7	7	32	54	1.65
4	4 % B 210	0.55	6	6	35	53	1.5
5	2 % B 210	0.70	3	3	46	48	1.05
6	0.2 % B 210	1.0	5	5	45	45	1.0
7	10 % K	0.03	7.5	7.5	65	20	0.3
13 <sup>a</sup>	10 % K	0.03	7.5	7.5	78	6	
2	10 % A	0.05	5	5	35	55	1.6

<sup>*a*</sup> From 3-methyl[6-<sup>13</sup>C]hexane isomerization.

Apart from catalysts of type B, two additional catalysts were investigated; one, 10 % A, which was prepared like B catalysts, behaved similarly. For the other, 10 % K, pretreated in oxygen at 770°C, the cyclic mechanism (EtCP) became predominant.

Isomerization of 3-methyl-[6<sup>-13</sup>C]hexane (I–W) and -[3<sup>-13</sup>C]hexane (I–T) was performed only for verification. For (I–W), only small amounts of n-heptane-[4<sup>-13</sup>C] were obtained, again showing that the abnormal mechanism and repetitive processes are not significant. Assuming the same contributions of bond-shift as for (I–X) isomerization, the contributions of (DMCP) and (EtCP) were calculated and are reported in table 4 : run 12, with 10% B 210, exactly reproduced run 3 and, in run 13, on 10% K, the same enhancement of (EtCP) was observed as in run 7. Similarly, in (I–T) isomerization (run 11 of table 3), the same contribution of (DMCP) yielding n-heptane [2<sup>-13</sup>C] (y = 50%) was found as in run 3 (50%).

## 2-METHYLHEXANES

Mass spectra of the 2-methylhexanes could be obtained only in a few experiments. Using the demethylated fragment and  $a_6$  made it possible to determine the concentration x' of 2-methyl-[1-<sup>13</sup>C]hexane and, in some cases, to deduce from x' the contributions of bond-shift and cyclic mechanisms. In table 5, run 11, performed with 3-methyl-[3-<sup>13</sup>C]hexane (I-T), shows the validity of the method; x' = 0 as expected (see table 1). Runs 1 and 14, with (I-X), demonstrate excellent reproducibility and run 15 demonstrates the extent of scrambling induced by a too high conversion. A dispersion effect is apparent from runs 1, 8 and 5; a decrease in the particle size drastically decreases the contribution of the bond-shift mechanism.

TABLE	5.—ISOMERIZATION	то	2-METHYLHEXANE

run	catalysts	H/Pt	reactant	$\alpha_{T}$	x'	bond- shift
1	10 % B 10	0.12	3-methyl[ <sup>13</sup> C]hexane (I-X)	15.2	61	22
14	10 % B 10	0.12	3-methyl <sup>13</sup> Chexane (I-X)	14.9	61	22
15	10 % B 10	0.12	3-methyl <sup>13</sup> C]hexane (I-X)	39.5	63	26
8	10 % B 210	0.35	3-methyl[1- <sup>13</sup> C]hexane (I-Z)	21.9	18	18
5	2 % B 210	0.70	3-methyl <sup>13</sup> Chexane (I–X)	19.6	48	0
11	10 🕉 B 210	0.35	3-methyl[3- <sup>13</sup> C]hexane (I-T)	16.0	0	
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**3-METHYLHEXANES (SELF ISOMERIZATION)** 

Five reaction mechanisms, two bond-shift mechanisms in which a methyl or propyl group is displaced (MeSh, PrSh) and three cyclic involving 1,2-dimethyl-, 1,3-dimethyl- or ethyl-cyclopentane intermediates (1,2-DMCP, 1,3-DMCP, EtCP) may account for the self-isomerization of 3-methylhexane. The various isotopic species obtained from the molecules labelled on carbons 1, 2, 3 or 6 and on the methyl group are reported in table 1: it should be recalled that in any cyclic mechanism at least one half of the self-isomerization products are labelled on the same carbon atom as the reacting molecule (fig. 1).

To determine the mole fractions of the various isotopic form x'', y'' etc., linear eqn (1')-(4') similar to eqn (1)-(4) were used. Any of eqn (1'), (2') or (3') in combination with eqn (4') allows the determination of one, or the sum of two, mole fractions.

For example, in the self isomerization of 3-methyl-[<sup>13</sup>C]hexane (I-X), concentrations z'' and x'' of (I-Z) and (I-X) were obtained from  $a_5$  and  $a_6$ , respectively, and the sum x'' + z'' from  $a_4$ .

$$z''a_{5z} + a_{5x}(u'' + w'' + x'') = z''a_{5z} + (1 - z'')a_{5x} = a_5$$
<sup>(2')</sup>

$$(x'' + z'')a_{4x} + (u'' + w'')a_{4u} = a_{4x}(x'' + z'') + a_{4u}(1 - x'' - z'') = a_4$$
(3')

$$x''a_{6x} + a_{6uwz}(u'' + w'' + z'') = x''a_{6x} + a_{6u}(1 - x'') = a_6.$$
<sup>(1')</sup>

Note (i) that in eqn (2') the  $a_5$  basis for (I–U) and (I–W) was assumed to be equal to the  $a_5$  basis for (I–X), the more abundant isotopic variety and (ii) that in eqn (1') an average value was used for  $a_6$ :  $a_{6uwz} = \frac{1}{3}(a_{6u} + a_{6w} + a_{6z})$ . The mole fractions thus obtained are reported in table 6, where comparison of column 7 and the sum of columns 5+6 shows the error in the calculations (< 15%).

From the mole fractions, the contribution of the various reaction mechanisms were estimated : propyl-shift and cyclic mechanism *via* 1,2-DMCP intermediate could not be distinguished and their sums were obtained from the self-isomerization of (I-X), (I-Z) and (I-T). The contribution of methyl shift may be calculated in the self-isomerization of (I-Z) and (I-W). Lastly, the cyclic mechanism involving 1,3-DMCP intermediate or the sums (1,3-DMCP)+(EtCP) and (1,3-DMCP)+(MeSh) were obtained from (I-W), (I-X) and (I-T), respectively. In order to compare the amounts of self-isomerized molecules with the amounts, reported in table 2, of molecules obtained by dehydrocyclization and apparent isomerization, the mole fractions y'', z'' etc. were multiplied by  $100-\alpha_{C_7}/\alpha_{C_7}$ , where  $\alpha_{C_7}$  represented the apparent conversion into C<sub>7</sub> hydrocarbons. Thus were obtained the numbers of self-isomerized

TABLE 6.—SELF-ISOMERIZATION OF 3-METHYLHEXANE

run	catalyst	H/Pt	αc7	(1)	(2)	(3)	$ \Delta\% ^a$	(PrSh)+ (1,2-DMCP)	(EtCP)	(1,3-DMCP)	(MeSh)
3-n	nethyl[13C]hexa	ne (I-X)								· · · · ·	
				z"	u'' + w''	1 - x''					
15	10 % B 10	0.12	29.1	7.2	4.6	10.2	15	17.5		11.2	
4	4 % B 210	0.55	17.2	2.2	2.1	4.5	4	10.6		10.1	
5	2 % B 210	0.70	17.9	1.45	2.45	3.5	11	6.7		11.2	
16	10 % B 10	0.12	53.2	10.7	15.4	21.4	20	9.4		13.5	
7	10 % K	0.03	15.7	5.7	2.3	8.9	10	30.6		12.3	-
3-met	hyl[1-13C]hexar	ne (I-Z)									
		. ,		<i>x</i> "	w**	x"+w"					
8	10 % B 210	0.35	18.2	3.0	4.5	6.9	8.5	13.5			20.2
9	2 % B 210	0.70	14.3	1.9	3.6	5.7	3.5	11.4			21.6
3-met	thyl[6-13C]hexar	ne (I-W)									
				<i>x</i> ″	z"	x'' + z''					
12	10 8/ B 210	0.25	12.0	1 15	205	1 65	75			77	25.0
13	10 % K	0.03	26.2	1.15	4.05	4.03 6.5	13		_	4.5	23.8 11.4
·	13Clb										
s-met	inyi[5-15C]nexai	1e (1-1)									
				<i>y</i>	u + v						_
11	10 % B 210	0.35	13.1	2.4	5.4			15.9		35.	8
						·	•	••• ·	······		
10 % B (runs 11, 12, 15)		17.5-	-0/2	3.5×2	7.7	×2	28.1	D,			
2 % B (runs 5, 9)		0.7-	-0/2	3.3×2	1.7	× Z	21.0	D			
п	5% K (runs 7, 1	3)	30.6-	-0/2	7.8×2	4.3	XZ	11.4		<b>D</b> )	
			(Pr	sn)	(EtCP)	(1,3-D	MCP)	(mesh) (	1,2-DMC	r)	
		···· _ · · · _ ·									

$$^{a}\Delta = \frac{(3)-(1)-(2)}{(3)} \times 100.$$

molecules with a label different from that of the reactant and corresponding to one hundred molecules of apparent reaction products: they are reported in the second part of table 6. With increasing metal dispersion from 0.12 to 0.70, there were important changes in reaction mechanisms. The respective decreases in the sum (PrSh)+(1,2-DCMP) and (MeSh) were from 17 to  $7\pm 3$  and from 28 to 21. On the other hand, the sum of the molecules by the two other cyclic mechanisms (1,3-DMCP) and (EtCP) remained constant.

Two experiments performed with the pretreated catalysts 10 % K show larger contributions of (1,2-DMCP) and/or of (PrSh) than in experiments with normal catalysts. Lastly, one experiment (run 16) is also presented in table 6 to show the extent of <sup>13</sup>C scrambling induced by too high conversion.

### **RELATIVE CONTRIBUTIONS OF BOND-SHIFT AND CYCLIC MECHANISMS**

From tables 1-6, the contributions of various isomerization pathways may be determined completely for two catalysts of extreme dispersion (10 % B 10 and 2 % B 210). In table 2 are reported the apparent  $C_7$  product distributions corresponding to runs 1 and 5. Tables 4 and 5 show distributions of n-heptane and 2-methylhexane among the different pathways. Lastly, the total number of molecules self-isomerized on catalysts 10 % B 10 and 2 % B 210 were calculated from the value reported in table 6, multiplying by 2 the values corresponding to cyclic mechanisms. In this calculation, the contributions of the various cyclic mechanisms were assumed to be independent of metal dispersion and no distinction was made between 10 % B 10 and 10 % B 210 catalysts. The number b of molecules self-isomerized according to mechanism (1,2-DMCP) was determined by dividing the percentage of 2,3-DMP by the ratio  $r_1 = 2,3$ -DMP/3-MH obtained in hydrogenolysis of 1,2dimethylcyclopentane ( $r_1 = 3.2$  and 1.5 on catalysts of low and high dispersion, respectively). Similarly the amounts of ethylpentane were estimated by dividing the percentage of n-heptane formed by the (EtCP) mechanism by the ratio  $r_2 = n$ -Hep/ EtP in ethylcyclopentane hydrogenolysis ( $r_2 = 1$  or 1.65).

A complete description of the various pathways is given in table 7, which includes rough and normalized data. The major differences between catalysts 10 % B 10 and 2 % B 210 resulted from the decrease in bond-shift reactions with increasing metal dispersion. For both catalysts, the ratio (1,2-DMCP+1,3-DMCP)/(EtCP) was equal to 4.8 and the ratio (1,3-DMCP)/(1,2-DMCP) equal to 1.6. On the other hand, in cyclopentane hydrogenolysis, a change in the metal dispersion altered the ratios r between the amounts of products obtained by breaking bonds with different properties, *i.e.*, bisecondary, secondary-tertiary and bitertiary. In table 8, the ratios obtained in 3-MH isomerization are compared with those obtained in  $C_7$  cyclopentanes hydrogenolysis. It is known that an increase in reaction temperature does not change the product distribution on highly dispersed catalysts and, on catalysts of low dispersion, significantly decreases the ratios such as  $r_4$  between bisecondary and secondary-tertiary C-C bond cleavage.<sup>7a</sup> Agreement between the two sets of results in table 8 is therefore excellent and shows the validity of our method of computation.

### DISCUSSION

Among the contact reactions of 3-methylhexane, hydrocracking and aromatization are irreversible and isomerization and dehydrocyclization are reversible. Consequently, the percentages of toluene and cracked molecules in the product distribution both increased with conversion. The former, however, increased twice as much as the latter because, while all  $C_7$  isomers are hydrogenolysed at comparable

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TABLE 7.—CONTRIBUTION OF VARIOUS PATHWAYS TO 3-METHYLHEXANE ISOMERIZATION

catalyst	10	% B 10	2 % B 210						
mechanisms	products	rough data <sup>a</sup>	normal <sup>b</sup> data/%	rough data <sup>a</sup>	normal <sup>b</sup> data/%				
chain lengthening	~~~~	1.8	1.05	1.1	0.7				
methyl shift	$\sim$	28.0	16.2	21.6	14.1				
propyl shift	$\sim$	16.1	9.3	1.55	1.0				
methyl shift		3.9	2.25	0	0				
total bond-shi		28.8		15.8					
	$\sim \sim \sim$	6.6	3.8	6.2	4.05				
	$\downarrow$	8.8	5.1	7.75	5.05				
(1, <b>2-DMCP</b> )	$\sim$	2.75	1.6	5.15	3.35				
	trans	18.9	10.95	19.85	12.95				
	cis	2.0	1.15	2.0	1.3				
total of (1,2-I	OMCP) mechanism		22.6 (31.7)		26.7 (31.7)				
	ĻĻ	9.0	5.2	8.9	5.8				
(1,3-DMCP)	$\sim$	13.8	8.0	15.5	10.1				
		15.4	8.9	15.4	10.05				
		24.6	14.25	25.85	16.85				
cis + trans									
total of (1,5-1	DWICP) mechanism		(51.0)		(50.8)				
	$\sim \sim \sim$	3.6	2.1	5.95	3.9				
(EtCP)	$\sim$	7.0	4.05	7.0	4.55				
	$\sum$	3.6	2.1	3.6	2.35				
	$\bigtriangleup$	7.0	4.0	6.0	3.9				
total of (EtC	P) mechanism		12.25 (17.2)		14.7 (17.5)				

<sup>*a*</sup> Calculated from tables 1, 4, 5 and 6. Number of converted molecules (isomerized, dehydrocyclized and self-isomerized) corresponding to 100 molecules of apparent reaction products; <sup>*b*</sup> as for footnote (*a*) but normalized to 100.

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rates, at least one is aromatized faster than 3-MH: 2-methylhexane and n-heptane, indeed, yield more aromatics than 3-methylhexane (7 and 14 % of the C<sub>7</sub> products instead of 4 %).<sup>8</sup> That the amounts of toluene were relatively irreproducible when compared with the amounts of other  $C_7$  products foreshadows a composite mechanism involving parallel pathways.<sup>8</sup> The percentage of toluene, however, did not seem to depend upon metal dispersion, indicating that all the elementary steps take place on a single type of site. Since toluene increases with temperature, at least one of these steps is more activated than any isomerization or hydrogenolysis reaction.<sup>8</sup>

reaction	catalyst	H/Pt	T/°C	$(1,2\text{-DMCP})$ $r_3 = \frac{3\text{-MH}}{\text{n-Hep}}$	(EtCP) $r_4 = \frac{3-\text{MH}}{\text{n-Hep}}$	$(1,3-\text{DMCP})$ $r_5 = \frac{2-\text{MH}}{3-\text{MH}}$
3-methylhexane	10 % B 10	0.12	340	0.4	1.95	0.9
isomerization	2 % B 210	0.7	360	0.85	1.15	1.0
cyclopentane	10 % $A^{a}$	0.04	280	0.3	3.8	0.95 <sup>b</sup>
hydrogenolysis	0.15 % A <sup>a</sup>	1.0	300	0.95	1.1	$1.3^{b}$

ABLE 8.—COMPARISON BETWEEN 3-MH ISOMERIZATION AND HYDROGENOLYSIS									
CYCLOPENTANES									

<sup>a</sup> Ref. (5). <sup>b</sup> 335°C [ref. (6)].

The distribution of hydrogenolysis products did not depend upon conversion:  $C_7$  hydrocarbons, then, must be cracked faster than hydrocarbons of lower molecular weight. This and the absence of any repetitive process in the adsorbed phase explain the small amounts of isobutane formed even at high conversion and the negligible contribution of extensive cracking to methane or ethane. That temperature and metal dispersion did not modify the product distributions suggests that there is only one mechanism, occurring on one single type of site.

Two mechanisms, differing in their activation energies, have been characterized for pentane and hexane hydrogenolysis at 250°C.<sup>9</sup> The contribution of the more highly activated one becomes predominant in 3-methylhexane hydrogenolysis at 360°C.

### **REVERSIBLE REACTIONS**

The decrease of cyclic molecules in the product distributions with increasing conversion may easily be accounted for by considering the simplified kinetic scheme 1, where reactant  $A_1$  yields only a single acyclic isomer  $A_2$  and one cyclic molecule  $A_3$ , via a common cyclic intermediate C. If it is assumed that all the reactions are pseudo

$$A_1 \underset{k_{-1}}{\overset{k_1}{\underset{k_{-1}}{\leftarrow}}} C \underset{k_2}{\overset{k_{-2}}{\underset{k_2}{\leftarrow}}} A_2$$
$$\overset{k_3 \uparrow \downarrow k_{-3}}{\underset{A_3}{\leftarrow}} A_3$$

SCHEME 1.

unimolecular <sup>10</sup> and if a steady-state approximation is used for C, the ratio  $\rho$  between cyclic and acyclic molecules is

$$\rho = \frac{k_{-3}}{k_3} \frac{k_2}{k_{-2}} \frac{1 - e^{-k_3 t}}{1 - e^{-k_2 t}}$$
(5)

where  $k_2$ ,  $k_3$ ,  $k_{-2}$  and  $k_{-3}$  represent pseudounimolecular rate constants. According to eqn (5),  $\rho$  is expected to decrease with contact time (or conversion) only if  $k_3$  is larger than  $k_2$ , which is the case, since  $k_3$  represents an adsorption and  $k_2$  a dehydrocyclization rate constant. Because of the large change in  $\rho$  with conversion, it is difficult to correlate the percentage of cyclic molecules to the amounts of acyclic isomers formed according to a cyclic mechanism. This consideration casts doubt upon any attempts to determine relative contributions of bond-shift and cyclic mechanisms by simply examining the product distributions.

Another reason for discarding the product distributions method is that it does not account for isomerization products having the same structure as the reactant. In the case of 3-methylhexane isomerization, because of the small amounts of "apparent" isomers formed by bond-shift (6 % on 10 % B 10 in table 7), the initial product distribution does not seem to vary noticeably with metal dispersion. However, when the self-isomerized molecules obtained by methyl and propyl shift are accounted for, which can only be achieved by using <sup>13</sup>C-labelled molecules, one notices that, with increasing metal dispersion, there is a decrease in the contribution of the bond-shift mechanism by a factor of two (from 30 to 15 %). 3-Methylhexane therefore behaves in isomerization very much like the other C<sub>7</sub> and C<sub>6</sub> hydrocarbons.<sup>1, 3</sup>

While the total percentages of bond-shift and the distribution of bond-shift isomers varied with metal dispersion, the relative contributions of the three cyclic mechanisms (bracketed in table 7) remained remarkably constant. Changes in the distribution of products obtained by a particular cyclic mechanism only result from the change in selectivity caused by breaking the various C—C bonds of the cyclopentane intermediate or/and from changes in the relative rates of desorption and ring cleavage. Thus may be explained the alteration with metal dispersion of the percentages of n-heptane formed by (1,2-DMCP) and (EtCP) mechanisms. Lastly, the ratio between cyclic and acyclic molecules in each cyclic mechanism is regulated by the structure of the cyclic intermediate. It is well known that hydrogenolysis of monosubstituted cyclopentane is faster than hydrogenolysis of disubstituted cyclopentane.<sup>11</sup> This difference explains why the relative percentages of acyclic isomers among the molecules obtained by (EtCP) mechanism were larger than those obtained by (DMCP) mechanisms.

### MECHANISMS OF 1,5 RING CLOSURE

Depending upon metal dispersion, two mechanisms, selective and non-selective, are involved in cyclic type isomerization and cyclopentane hydrogenolysis.<sup>7</sup> On highly dispersed catalysts, the non-selective cyclic mechanism of isomerization interconverts 2-methylpentane and n-hexane, but not 2,2-dimethylpentane and 2-methylhexane,<sup>1</sup> and quaternary-secondary C—C bonds cannot be ruptured in non-selective hydrogenolysis of *gem*-dimethylcyclopentane.<sup>11</sup> Dicarbene recombination <sup>12</sup> could account for these facts (scheme 2), see page 1750.

On catalysts of low dispersion, the selective cyclic mechanism allows interconversion between 2-methylpentane and 3-methylpentane, but not between methyl pentanes and n-hexane,<sup>7</sup> and the tertiary-secondary bonds do not rupture in selective hydrogenolysis.<sup>6, 7</sup> One might suggest for dehydrocyclization, a dicarbyne recombination mechanism yielding  $\alpha\alpha\beta\beta$  tetra-adsorbed species (scheme 3), see page 1750.

HYDROCARBON ISOMERIZATION ON  $Pt-Al_2O_3$ 





Although metallocarbynes have been isolated,<sup>13</sup> dicarbyne recombination has no analogue in coordination chemistry. This could be because the geometry of a 1,5-dicarbyne intermediate requires the participation of two well separated metal atoms and no attempt has yet been made to obtain complexes of this type. However, the structure, binuclear or mononuclear, of the precursor species in selective and non-selective cyclic mechanisms would explain, on simple geometrical grounds, the effect of metal particle size. If it is assumed that any isomerization reactions take place on edge atoms,<sup>3</sup> then on catalysts with large metal particles, two edge atoms would be available for dicarbyne formation and the cyclic mechanism would be selective. On the other hand, on highly dispersed catalysts, the only possible mechanism would be that involving a single atom, *i.e.*, dicarbene recombination.

The relative contributions of the three cyclic mechanisms (EtCP), (1,2-DCMP) and (1,3-DMCP) are the same on catalysts of either very low or very high dispersion.

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Therefore a common initial step must be involved in selective and non-selective cyclic mechanisms, regulating the distribution of the reacting molecule between the three dehydrocyclization pathways. This common step, we believe, is the rearrangement of a  $\pi$ -olefinic species (b) into metallocarbene (c) by hydrogen transfer (scheme 4), see page 1750.

The reverse of this reaction, metallocarbene isomerization,<sup>14</sup> is very fast so that between (b) and (c) an equilibrium is probably reached, the position of which depends upon the degree of double bond substitution. The most stable adsorbed olefins,  $\alpha\alpha$ disubstituted or  $\alpha\alpha\beta$  trisubstituted ethylene, would then isomerize much less readily than other adsorbed olefins. In fig. 6 are represented all the possible pathways leading from a  $\pi$ -adsorbed species to a cyclic molecule *via* metallocarbene and dicarbene. Among these paths, two,  $B_1$  and  $B_3$ , are less favoured on account of the



FIG. 6.—All possible pathways from a  $\pi$ -adsorbed species to a cyclic molecule *via* metallocarbene and dicarbene.  $B_1$  and  $B_3$  are unfavoured paths.

higher stability of the  $\pi$ -adsorbed olefin. Although electronic and steric factors arising from the structure of the transition state are certainly involved, it is interesting to note that the contributions of the cyclic mechanisms (EtCP), (1,2-DMCP) and (1,3-DMCP), obtained from fig. 6 when neglecting  $B_1$  and  $B_3$  and supposing all other pathways to be equivalent, are very close (1:2:3) to those that are actually obtained (1:1.85:2.95).

The mechanisms proposed herein explain all the major features of dehydrocyclization: (1) the selectivity on catalysts of low and high metal dispersion, (2) the very high negative orders with respect to hydrogen in the case of hexane and pentane cyclic-type isomerization and (3) the contribution of various parallel pathways in the case of a complex molecule.

Three alternative mechanisms had been proposed previously for 1,5 ring closure. The first, C (sextet-doublet mechanism), involves simple 1,5 ring closure and a physically adsorbed transition state.<sup>15, 16</sup> If one neglects any steric hindrance, this mechanism would result in equal contributions from (EtCP), (1,2-DMCP) and (1,3-DMCP) (scheme 5). It would favour (EtCP), if one assumes that all seven carbon atoms are in contact with the surface in configurations b and c.<sup>17</sup>



The second mechanism, D, involves  $1,2\pi$ -olefinic, 5- $\sigma$ -triadsorbed species and consists of a cis-olefin insertion in a carbon-metal bond.<sup>18</sup> This mechanism, represented in scheme 6, is almost the same as that proposed by Herrington and Rideal for 1,6 ring closure.<sup>19</sup> For 3-methylhexane, it would yield contributions (1:1:1) or (1:1:2) for the three dehydrocyclization pathways, according to whether all  $D_i$  species are

equivalent or a steric effect eliminates species  $D_1$  and  $D_3$ .



A third mechanism, E, involves axe triadsorbed species as precursor and consists of a carbene insertion in a carbon-metal bond (scheme 7). It was preferred to D for

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non-selective ring closure because it explains the equal rates found on platinum films for the de-hydrocyclization of 2,2,4-trimethyl-, 2,2,3-trimethyl- and 2,2,4,4-tetramethyl-pentanes.<sup>20</sup>



SCHEME 7.—Mechanism E.

From all these mechanisms only those involving metallocarbene precursors, A, B and E, account for the product distributions in 3-methylhexane isomerization. Like A, E has an analogue in coordination chemistry <sup>21</sup> but unlike A none of mechanisms C, D and E explains simply the non-formation of gem-disubstituted cyclopentanes.

### MECHANISMS OF BOND-SHIFT

Distinctions have been made, among the bond-shift reactions, between chain lengthening or chain shortening and alkyl shifts.<sup>9</sup> For small molecules, isopentane and 2-methyl- and 3-methylpentanes, the latter are largely predominant, as are two of the alkyl shifts, reactions (11) and (12) in 3-methylhexane isomerization. On the other hand, isomerization of 3-methylhexane to 2-methylhexane, reaction (10), the reverse reaction <sup>1b</sup> and the isomerization of 2,3-dimethylpentane to 2,4-dimethylpentane <sup>1a</sup> all have rates comparable with chain lengthening. Any mechanism for alkyl should account for these structural effects.

Four mechanisms for bond-shift reactions have so far been proposed. Two are similar and involve the same precursor,  $\alpha\alpha\gamma$  triadsorbed species but two different transition states, either a Dewar-type  $\pi$ -complex <sup>22</sup> or an adsorbed cyclopropane <sup>23</sup> (scheme 8).



Substituent effects are expected to be the same or very similar in both mechanisms. If one assumes, as suggested by *ab initio* calculations,<sup>24</sup> that cyclopropane is stabilized by methyl groups, the following orders should be found for alkyl shifts in 3-methyl-hexane: c > a > b (scheme 9) instead of the one actually observed,  $c = b \ge a$ : mechanisms F and G should then be rejected.

A third mechanism, *H*, proposed by Rooney *et al.* assumes 1,2 alkyl shift *via* a transient species involving three-centre orbital as in non-classical carbonium ions.<sup>25</sup>

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SCHEME 9.

Such a mechanism would account for the observed results only if the symmetry of the transition state plays an important role (scheme 10). If the rates are influenced primarily by the nature of the shifted alkyl, the major differences should not be between reaction a and reaction b or c, but rather between methyl shift a or b and propyl shift c.



Moreover, mechanism H accounts for structural effects in chain lengthening,<sup>1b</sup> a reaction which is well differentiated from alkyl shift.

A fourth mechanism, J, proposed recently <sup>9</sup> is specific to alkyl shift, involving metallocyclobutane as precursor and a transition state which consists of a carbenoid species similar to the one proposed later on for phenylmetallocyclobutane rearrangement <sup>26</sup> except that several metal atoms are required instead of one. An alternative description of mechanism J, which is in better agreement with coordination chemistry, is represented in scheme 11.



Mechanism J' in scheme 11 is the same as that proposed by Chauvin and Herrisson <sup>27</sup> for metathesis, except that two metal atoms are involved instead of one, thus accounting for the minimal particle size required for methyl shift.<sup>4</sup> Mechanism J' readily explains, in the case of 3-MH and 2,3-DMP isomerization, the differences in rates between the various alkyl shifts. Indeed, free rotation of the olefinic group in step 2 requires an activation energy of  $\approx 15$  kcal mol<sup>-1</sup>,<sup>28</sup> an amount which could differ by a few thousand calories if small substituents are replaced by bulky ones (scheme 12). Since a change in activation energy of 3 kcal would reduce the rate by a factor of 10 at 600 K, this effect is sufficient to account for the observed rate: reactions a and d, where the  $\pi$ -olefinic species are substituted by propyl and isopropyl groups, are less favoured than reactions b and c.

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In conclusion, detailed analysis of the various parallel pathways in 3-methylhexane isomerization shows structural effects which are best interpreted by assuming carbene intermediates. The effect of metal-particle size on the relative contributions of the various reaction mechanisms, non-selective cyclic, selective cyclic and bond-shift mechanisms, has been explained simply in preceding papers by rough geometrical considerations, *i.e.*, assuming participation of one or several surface metal atoms. Since the reactivities of metallocarbenes are strongly influenced by the electronic properties of the metal, it is possible that this effect only reflects the change in electronic properties which results from a change in metal-particle size.<sup>29</sup> This possibility is strengthened by the drastic changes in reaction mechanisms that are observed with changes in the nature of metal in supported catalysts of comparable metal-particle size.<sup>30-32</sup>

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