As shown in Figures 2 and 3, the addition of a methylene group to 2,3-dimethylbutane increases the reactivity of the molecule. For 50 mole % conversion of 2,3-dimethylpentane a reaction temperature of approximately 310° C. is necessary compared to 350° C. for the same conversion of 2,3-dimethylbutane. However, the substitution of a methyl group for a secondary hydrogen atom in 2,2-dimethylbutane does not result in as large a change in the reactivity of the molecule. The data show that 2,2,3-trimethylbutane requires a reaction temperature of approximately 20° C. lower than 2,2-dimethylbutane for the same conversion.

The data presented in the previous paper on *n*-hexane and that shown in Tables III and IV reveal that the initial products formed in the isomerization of *n*-hexane, *n*-heptane, and *n*-octane are the methyl isomers. *n*-Hexane isomerizes to 2- and 3-methylpentanes; *n*-heptane to 2- and 3-methylhexanes; and *n*-octane to 2-, 3-, and 4-methylheptanes. These results substantiate the conclusions of Evering and Waugh (12) that the isomerization reaction occurs in a stepwise manner. For *n*-hexane the isomerization to the isomers appears to occur as shown herewith.

Since the isomerization of 3-methylpentane was not investigated, the direct formation of 2,2-dimethylbutane from this isomer is not indicated.

The data contained in Tables III and IV show that hydro-



cracking of the heptanes and octanes at the higher conversions results primarily in the formation of propane, butanes, and pentanes. The absence of substantial amounts of methane and ethane reveals that cracking of these hydrocarbons occurs primarily at the center of the molecules. Thus the nickel-silica-alumina catalyst does not show the typical demethanation reaction of nickel-containing catalysts (22). This behavior of the nickelsilica-alumina catalyst is similar to that observed by several investigators (8, 16) in the catalytic cracking of alkane hydrocarbons in the presence of silica-alumina-zirconia catalysts. The pronounced tendency of these catalysts to form butanes and pentanes in the cracking of higher molecular weight hydrocarbons is well known.

(Isomerization of Saturated Hydrocarbons) CYCLOALKANES

F. G. CIAPETTA¹

THE activity of the standard nickel-silica-alumina catalyst was further investigated for the isomerization of cycloalkane hydrocarbons. These include methylcyclopentane, cyclohexane, methylcyclohexane, and ethylcyclohexane. Under conditions similar to those employed for the alkane hydrocarbons, this catalyst was found to be quite active and highly selective for the isomerization of these cycloalkanes. The formation of 1,1dimethylcyclopentane from methylcyclohexane and 1,1-dimethylcyclohexane and 1,1,2-trimethylcyclopentane from ethylcyclohexane in appreciable yields shows that the cycloalkanes containing a quaternary carbon atom are normal products of the isomerization of the alkylcyclohexanes (21).

EXPERIMENTAL

The apparatus, experimental procedure, reaction conditions, and method of analysis were similar to those described in the first paper of this series (p. 147). The standard nickel-silicaalumina catalyst was used in this investigation.

Methylcyclopentane (95% purity) and cyclohexane (99% purity) were obtained from the Phillips Petroleum Corp. Methylcyclohexane and ethylcyclohexane were of 99% purity and were obtained from Eastman Kodak Corp. Each of these hydrocarbons was analyzed by the mass spectrometer in order to calculate conversion and isomer yields on the basis of the pure compound.

EXPERIMENTAL RESULTS

Methylcyclopentane. The isomerization of methylcyclopentane in the presence of the standard nickel-silica-alumina catalyst was investigated over the temperature range of 280° to 370° C. The experimental data are given in Table I. The molar conversion of methylcyclopentane as a function of the reaction temperature is plotted in Figure 1.

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Analysis of the reaction products revealed that isomerization to cyclohexane was the predominant reaction at all conversions, but at the higher reaction temperatures, hydrocracking to hexanes and lower molecular weight hydrocarbons and isomerizationdehydrogenation to benzene also occur. The selectivity factor (molar ratio of isomer yield to methylcyclopentane conversion) is high initially, having a value of 0.97, which drops off to 0.65 at the highest conversion.

Since side reactions are not too extensive, the apparent low reactivity of methylcyclopentane is understandable from the standpoint of the equilibrium concentrations of methylcyclopentane and cyclohexane at these conditions. In Table II are the observed and calculated (29) values for methylcyclopentane and cyclohexane. Comparison of these values show that the observed concentrations of cyclohexane and methylcyclopentane obtained above 316° C. are in good agreement with the calculated values.

Cyclohexane. The data shown in Table I and plotted in Figure 1 reveal that cyclohexane is selectively isomerized to methylcyclopentane in the presence of the standard nickel-silica-alumina catalyst. Because of a partial hydrogen failure prior to run 626, the conversion decreased at the highest temperature studied. The selectivity factor at the highest conversion obtained—i.e., 76.9%—is 0.95 showing that side reactions are not too extensive under these conditions. At this conversion only 2.4 mole % of the cyclohexane is converted to hexanes and lower molecular weight alkane hydrocarbons, and 1.9 mole % is dehydrogenated to benzene. Hydrocarbons higher in molecular weight than the feed were not found.

As shown in Table II, the observed mole per cent concentrations of cyclohexane and methylcyclopentane were rapidly approaching the calculated equilibrium values as the reaction temperature was increased. However, due to the decrease in the catalyst activity prior to run 626, the equilibrium concentrations were

TABLE I. ISOMERIZAT	FION OF	METH	YLCYCI	LOPENI	ANE .	and C	YCLOHI	EXANE
Cat Pre L.S H ₂ /	alyst = ; ssure = ; V. = ; HC = ;	standaro 24.8 atn 1.0 vol./ 4	l nickel- vol./hr.	-silica-al	umina			
Run No. Temperature, ° C.		$\substack{628\\316}$	$\begin{array}{c} 629 \\ 344 \end{array}$	$630 \\ 371$	$\begin{array}{c} 623 \\ 287 \end{array}$	$\begin{array}{c} 624 \\ 342 \end{array}$	$\frac{625}{371}$	$\begin{array}{c} 626 \\ 390 \end{array}$
charge Cycloalkane	88.0 Me	91.3 ethyleye	90.9 lopentar	92.9 ne <u></u>	98.3	96.0 -Cycloh	96.5 exane	97.7
Product distribution, moles Methane Ethane Propane Isobutane n-Butane Isopentane n-Pentane Hexanes Methylcyclopentane Cyclohexane Benzene	/100 mole 0.4 89.5 10.2 0.1	s of cha 0.6 0.4 0.4 0.9 86.9 11.7 0.1	rge (no- 0.4 0.1 0.1 0.2 2.6 82.1 14.5 0.3	loss bas: 0.6 1.0 0.3 0.9 0.5 2.2 80.0 12.9 1.8	is) 8.5 91.5 0.1	0.4 68.9 30.7 0.5	0.4 0.3 0.1 0.6 0.2 1.2 72.6 23.1 1.9	$\begin{array}{c} 0.5\\ 0.8\\ 0.8\\ 1.0\\ 0.9\\ 0.5\\ 29.8\\ 31.5\\ 3.6 \end{array}$
Mole % of charge Convn. of charge Isomer yield	$\begin{smallmatrix}10.5\\10.2\end{smallmatrix}$	$\substack{13.1\\11.7}$	$\substack{17.9\\14.5}$	$\substack{20.0\\12.9}$	8.5 8.5	$69.3 \\ 68.9$	$76.9 \\ 72.6$	68.5 59.8
Selectivity factor Wt. % C on catalyst	0.97	0.89	0.81	$\begin{array}{c} 0.65 \\ 0.32 \end{array}$	1.0	0.99	0.95	$\begin{array}{c} 0.87\\ 0.36 \end{array}$



not obtained. More recent data have shown that these catalysts will give the equilibrium concentrations of these cycloalkanes under suitable reaction conditions.

Methylcyclohexane. The experimental data for the isomerization of methylcyclohexane are shown in Table III. The conversion of this hydrocarbon increases rapidly over the temperature range 280° to 370° C. This is shown in Figure 1 which indicates that methylcyclohexane is slightly more reactive than cyclohexane up to conversions of 50 to 60 mole % and slightly less reactive at higher conversions.

Isomerization is the primary reaction up to methylcyclohexane conversions of approximately 70 mole %. The observed selectivity factor at a conversion of 67.4 mole % is 0.93 and decreases to 0.83 at a conversion of 72.7%. Analysis of the products showed that all the possible isomers are formed at the reaction temperatures investigated. Since the mass spectrometer cannot differentiate between the cis and trans isomers of 1,2- and 1,3-dimethylcyclopentanes the concentration of these isomers is not known. The appearance of 1,1-dimethylcyclopentane in the reaction products at the lowest conversion—i.e., 22.7% indicates that the formation of this isomer containing a quaternary carbon atom occurs readily in the presence of this catalyst. At the higher reaction temperatures, dehydrogenation of methylcyclohexane to toluene and hydrocracking to form heptanes and lower molecular weight alkanes occur to a small extent.

The similarity in the concentrations of the isomers produced at 342° and 370° C. suggests that under these conditions equilibrium may have been established among the isomers. In Table IV are shown the experimentally observed molar concentrations of each of the isomers and those calculated from the thermodynamic data of Rossini and coworkers (10). The good agreement of the experimental values with those calculated show that the equilibrium concentrations of each of the isomers is obtained under these conditions.

Ethylcyclohexane. The number of isomers of ethylcyclohexane can be large because of isomerization reactions involving the side chain to form dimethylcyclohexanes; the contraction of the six-membered ring to a five-membered ring to form the methylethylcyclopentanes and n-propylcyclopentane; or both the side chain and the ring to form the trimethylcyclopentanes. The 1,1-dimethylcyclohexane isomer may further isomerize to form isopropylcyclopentane. The cis and trans isomers of some of these cycloalkanes could also be formed.

The experimental data for the isomerization of ethylcyclohexane are given in Table V. As shown in Figure 1, this hydrocarbon is more re-

active than cyclohexane and methylcyclohexane at the same reaction temperature.

Analysis of the reaction products showed that isomerization is the primary reaction in the presence of the standard nickel catalyst. The selectivity factor for isomerization is 0.92 at 58.9 mole % conversion, and still 0.83 at 81.3% conversion. The selectivity drops off at the highest conversion reached—i.e., 84.3%—owing to an increase in the hydrocracking reaction and

TABLE II. EQUILIBRIUM CONCENTRATIONS OF METHYLCYCLOPENTANE AND CYCLOHEXANE

			Concentratio	on, Mole %			
		Methylcy	clopentane	Cyclob	Cyclohexane		
Temperature, C,		Exptl.	Caled, (29)	Exptl.	Caled. (29)		
	А.	Methylcyd	elopentane \rightarrow Cy	clohexane			
$288 \\ 316 \\ 344 \\ 371$		89.8 88.1 85.0 86.1	$82.1 \\ 84.4 \\ 86.2 \\ 87.7$	10.2 11.9 15.0 14.9	$17.9 \\ 15.6 \\ 13.8 \\ 12.3$		
	в.	Cyclohexa	ane \rightarrow Methylcyc	lopentane			
$287 \\ 342 \\ 371$			$81.9 \\ 86.2 \\ 87.7$	$91.5 \\ 30.8 \\ 24.2$	$ \begin{array}{r} 18.1 \\ 13.8 \\ 12.3 \end{array} $		

TABLE III. ISOMERIZATION OF METHYLCYCLOHEXA	NE
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Run No. Temperature, °C. Total recovery, wt. % of charge	$619 \\ 286 \\ 96.0$	$\begin{array}{c} 620 \\ 313 \\ 96.3 \end{array}$	$\substack{\begin{array}{c} 621\\ 342\\ 99.7 \end{array}}$	$622 \\ 370 \\ 97.4$
Product distribution, moles/100 mole Ethane Propane Isobutane n-Butane n-Pentane Heptanes 1,1-Dimethyloyclopentane 1,3-Dimethyloyclopentane Ethyloyclopentane Ethyloyclopentane Methyloyclohexane Toluene	es of charge (1.2 0.1 1.3 6.4 6.2 8.0 77.3 0.1	no-loss b 0.4 0.3 0.1 4.8 18.3 13.6 10.2 52.5 0.2	asis) 0.9 0.8 0.8 0.8 1.1 7.6 23.2 22.6 9.3 32.6 1.5	$\begin{array}{c} 0.3\\ 0.9\\ 1.2\\ 2.28\\ 1.1\\ 2.18\\ 21.0\\ 22.8\\ 21.0\\ 22.8\\ 27.3\\ 6.2\end{array}$
Mole % of charge Convn. of charge Isomer yield Selectivity factor Wt. % C on catalyst	22.7 21.9 0.97	$47.5 \\ 46.9 \\ 0.99 \\ \dots$	$67.4 \\ 62.7 \\ 0.93 \\ \dots$	72.7 60.3 0.83 0.32
nt. 76 C on catalyst				0.

. .

TABLE	IV.	EQUILIBRIUM	Con	ICEN	TRATIONS	OF
Me	THYL	CYCLOHEXANE	AND	Its	Isomers	

	Concentration, Mole %					
	342° C.		3	370° C.		
	Exptl.	Caled. (10)	Exptl.	Calcd. (10)		
1,1-Dimethylcyclopentane 1,2-Dimethylcyclopentane 1,3-Dimethylcyclopentane Ethylcyclopentane Methylcyclohexane	$8.0 \\ 24.3 \\ 23.7 \\ 9.8 \\ 34.2$	9.220.323.510.536.5	$8.9 \\ 24.0 \\ 25.8 \\ 10.2 \\ 31.2$	$9.1 \\ 21.2 \\ 25.2 \\ 11.8 \\ 32.7$		

TABLE V. ISOMERIZATION	ог Етну	LCYCLOR	EXANE	
Catalyst = standard r Pressure = 24.8 atm. L.S.V. = 1.0 vol./vo H ₂ /HC = 4	nickel-silica ol./hr.	a-alumina		
Run No. Temperature, [°] C. Total recovery, wt. % of charge	663 286 99,5	$\begin{array}{c} 664 \\ 317 \\ 94.1 \end{array}$	$\begin{array}{c} 665 \\ 343 \\ 95.7 \end{array}$	$\begin{array}{r} 666 \\ 372 \\ 98.1 \end{array}$
Product distribution, moles/100 moles of charge (no-loss basis) Ethane Propane Isobutane <i>n</i> -Butane Isopentane <i>n</i> -Pentane Hexanes Octanes Cyclohexane Methylcyclopentane 1,2,3-Trimethylcyclopentane Isopropylcyclopentane Ingrathylcyclopentane	0.4 0.5 0.2 2.4 0.6 2.3 1.4 6	0.5 0.6 0.6 2.8 7.8 1.7 7.8 1.3 8	$\begin{array}{c} 1.0\\ 2.5\\ 0.6\\ 1.1\\ 0.2\\ 2.9\\ 1.1\\ 2.6\\ 12.4\\ 0.5\\ 12.0\end{array}$	$\begin{array}{c} 0.4\\ 4.6\\ 8.1\\ 4.5\\ 4.0\\ 1.4\\ 5.3\\ 3.5\\ 0.31\\ 2.6\\ 11.3\\ 0.7\end{array}$
1,2-Dimethylgyclohexane Ethylgyclohexane Benzene Toluene Ethylbenzene plus xylenes	11.0 78.4 0.1	$\begin{array}{c} 35.0 \\ 41.1 \\ 0.1 \\ 0.1 \\ 0.6 \end{array}$	$ \begin{array}{c} 12.0 \\ 40.0 \\ 18.7 \\ 0.3 \\ 0.5 \\ 3.0 \end{array} $	28.0 15.7 0.7 1.9 7.8
Mole % of charge Convn. of charge Isomer yield	$\begin{array}{c} 21.6 \\ 18.9 \end{array}$	58.9 53.9	$ 81.2 \\ 67.5 $	$ 84.3 \\ 51.7 $
Selectivity factor Wt. % C on catalyst	0.88	0.92	0.83	$0.61 \\ 0.37$

dehydrogenation to aromatics. The isomers formed are primarily the dimethylcyclohexanes and trimethylcyclopentanes indicating that the isomerization involves both the side chain and the ring. Although 1,1- and 1,2-dimethylcyclohexanes were the only dimethylcyclohexanes identified, small amounts of the 1,3- and 1,4- isomers may be present. Of the possible trimethylcyclopentanes, only 1,1,2- and 1,2,3-trimethylcyclopentanes were found. Isopropylcyclopentane was also definitely established in small concentrations in the products. The absence of methylethylcyclopentanes is significant from the standpoint of the formation of the trimethylcyclopentanes.

At the higher reaction temperatures, hydrocracking of the side chain and the ring occurs to form octanes and lower molecular weight alkanes and cycloalkanes. Dehydrogenation of the cyclohexanes also occurs at these higher temperatures to form the corresponding aromatic hydrocarbons.

DISCUSSION

The literature on the isomerization of cycloalkanes is too extensive to review in this paper (?). At low temperatures $(25^{\circ} \text{ to } 150^{\circ} \text{ C.})$ aluminum chloride and bromide are the most active catalysts for the selective isomerization of methylcyclopentane and cyclohexane. Several investigators have reported the isomerization of cycloalkanes at higher temperatures $(350^{\circ} \text{ to } 500^{\circ} \text{ C.})$ in the presence of molybdenum sulfide and oxide (?) or tungsten sulfide (37) catalysts under hydrogen pressures of the order of 100 to 300 atmospheres. In the latter case, hydrocracking reactions are quite extensive resulting in poor selectivity for the isomerization. Recently, Haensel and Donaldson (21) have reported the isomerization of methylcyclohexane in the presence

of hydrogen and a platinum containing catalyst. The isomerization of cyclohexane and methylcyclopentane in the presence of a dual functional catalyst has been recently reported by Heinemann and his coworkers (23).

The formation of 1,1-dimethylcyclopentane from methylcyclohexane and 1,1-dimethylcyclohexane and 1,1,2-trimethylcyclopentane from ethylcyclohexane is rather interesting. The isomerization of methylcyclohexane to 1,1-dimethylcyclopentane may occur by two paths:

Contraction of the ring



or by further isomerization of ethylcyclopentane



At the lowest conversion of methylcyclohexane, both 1,1-dimethyl and ethylcyclopentanes are present indicating that these cycloalkanes may be primary products of the isomerization. Thus, it appears more likely that 1,1-dimethylcyclopentane is formed by Reaction 1 rather than Reaction 2. However, further work at lower conversions of methylcyclohexane is necessary to definitely establish this reaction.

The primary products previously observed in the isomerization of ethylcyclohexane are the dimethylcyclohexanes (7). Although trimethylcyclopentanes and isopropylcyclopentane are also present at the lowest conversion of ethylcyclohexane (Table V), the stepwise nature of the isomerization reaction precludes their formation as primary products. The complete absence of methylethylcyclopentanes is in agreement with the results obtained by other investigators (7). The isomers found in the present investigation indicate that the isomerization of ethylcyclohexane may proceed by Reaction 3 or 4.



Hence, 1,1,2-trimethylcyclopentane may result from both the isomerization of 1,1-dimethylcyclohexane or 1,2-dimethylcyclo-

hexane. Schuit and his coworkers (43) found that 1,1-dimethylcyclohexane isomerizes in the presence of aluminum chloride at 80° C. to give only the dimethylcyclohexanes. However, it cannot be concluded that these isomers are the only ones formed at higher reaction temperatures since the equilibrium is more favorable for the formation of alkylevelopentanes. Furthermore, in order to explain the formation of isopropylcyclopentane, it is necessary to conclude that 1,1-dimethylcyclohexane can isomerize further to form a five-membered ring isomer since the direct

formation of isopropylcyclopentane from any of the other isomers is highly improbable.

The production of aromatic hydrocarbons at the higher reaction temperatures shows that the hydrogenation agent, nickel, retains its ability to catalyze the dehydrogenation of cyclohexanes. Hence, in the presence of this catalyst the direct production of aromatic hydrocarbons in high yields from alkylcyclopentanes by simultaneous isomerization and dehydrogenation may be possible at higher temperatures than those used in the present investigation,

(Isomerization of Saturated Hydrocarbons)

NATURE OF THE CATALYST AND MECHANISM **OF THE REACTION**

F. G. CIAPETTA¹

N THE previous papers of this series it has been established that on combining a hydrogenation catalyst with a silicaalumina cracking catalyst, a complex catalyst is obtained which is very active and highly selective for the isomerization of saturated hydrocarbons.

Early in this investigation it was observed that the introduction of sodium ions, by an exchange reaction, into the catalyst during its preparation poisoned the catalyst for the isomerization reaction. The results of these experiments and the significance of the poisoning effect of sodium in relation to the chemical nature of the isomerization catalyst and the mechanism of the reaction are described in this paper.

Also included are the results obtained on passing 1-pentene and 1-hexene over the standard nickel-silica-alumina catalyst in the presence of excess hydrogen. The rapid hydro-isomerization of these alkenes at lower reaction temperatures than previously found for the corresponding saturated hydrocarbons, suggests that the initial and rate-controlling step in the isomerization of saturated hydrocarbons is the dissociation of a carbonhydrogen bond at the metal surface. Consideration of all the factors involved suggests that the mechanism of the isomerization reaction involves the formation of carbonium ions on the surface of the catalyst.

EXPERIMENTAL

The apparatus, experimental procedure, preparation of the standard nickel-silica-alumina catalyst, reaction conditions, and method of analysis were similar to those described in the first paper of this series (p. 147). The alkenes, 1-hexene, and 1pentene (95% purity) were obtained from Humphrey-Wilkinson, Inc. Each of these hydrocarbons was analyzed by the mass spectrometer in order to calculate conversions and isomer yields on the basis of the pure compound.

Catalyst SA-5N (I) was prepared by rapidly mixing 750 ml. of a hot (90° C.) solution of sodium carbonate (78.5 grams of $N_{a_2}CO_8$) with 750 ml. of a hot (90° C.) solution of nickel nitrate [148.9 grams of Ni(NO₈)₂·6H₂O]. To the resulting mixture was added 570 grams of fresh, ground synthetic silica-alumina catalyst. The slurry was stirred for 10 minutes and filtered; the cake was washed five times (each water wash was 1500 ml.), and then dried at 110° C. for 16 hours. The amount of sodium carbonate used represents a 45% excess over the theoretical requirement. This catalyst contained 1.24% sodium by weight. Catalyst SA-5N (V) was prepared in a manner similar to that used for the standard nickel-silica-alumina catalyst.

EXPERIMENTAL RESULTS

Effect of Sodium. The experimental data for the reaction of n-hexane in the presence of catalyst SA-5N (I) are shown in Table I. At reaction conditions similar to those used with the standard nickel-silica-alumina catalyst, the products obtained revealed that the catalyst prepared in the presence of sodium ions showed little activity for the isomerization of n-hexane. The main products formed were hydrocarbons of lower molecular weight due to hydrocracking reactions. The large amounts of methane produced revealed that this catalyst was active for selective demethylation of n-hexane. The predominance of n-pentane and n-butane in the products showed that little isomerization of *n*-hexane occurred prior to demethylation.

In order to determine if sodium ions would also poison an active isomerization catalyst, catalyst SA-5N (V) was soaked in a 10% solution of sodium carbonate, washed free of absorbed sodium ions, and dried at 110° C. Chemical analysis of the catalyst showed it contained 2.02% by weight of sodium. Table I gives the results obtained with *n*-hexane for this catalyst prior to treating with sodium carbonate solution and after treating. The sodium-poisoned catalyst was active primarily for hydrocracking reactions and the products formed were similar to those obtained using catalyst SA-5N (I).

Hydro-Isomerization of Alkenes. The hydrogenation of 1-pentene and 1-hexene in the presence of the standard nickelsilica-alumina catalyst was investigated to determine if skeleton isomerization occurs simultaneously with hydrogenation. These alkenes were contacted with the catalyst under conditions similar to those used for the isomerization of saturated hydrocarbons. Preliminary experiments showed that rapid hydrogenation occurred at low temperatures, and because of the exothermic nature of the reaction, the temperature of the upper portion of the catalyst bed increased from 50° to 85° C. above the furnace block temperature.

The results obtained with these alkenes are shown in Table II. Included in the data are the highest and lowest temperatures observed in the catalyst bed. The reaction products were completely saturated. The conversions of the alkenes are based on the concentrations of the corresponding saturated hydrocarbon in the products.

The conversions of 1-pentene and 1-hexene as a function of the highest observed catalyst temperature are shown in Figures 1 and 2. Also shown for comparison purposes are the results previously obtained for n-pentane and n-hexane over the same catalyst. The data show that the conversion of alkene hydro-

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