taken up in benzene. The organic extracts were in all cases made up to fixed volumes, and aliquots were taken for analysis.

Chromatographic separations were done on 1-cm. diameter 42-cm. columns containing approximately 20 g. of fresh 60–100 mesh Florisil (Floridin Co., Tallahassee, Fla.). The columns were developed and eluted at an average flow rate of 4 ml. per min., using first carbon tetrachloride, then mixtures with chloroform in volume ratios of 9:1, 8:2, 7:3, 6:4, 1:1, and finally pure chloroform. The eluate was collected in fractions of 20 or 30 ml. in tared flasks. Each fraction was evaporated in a stream of filtered air and then dried *in vacuo* for at least 12 hr. before weighing the residues and determining their melting points. The order of elution was invariably O-alkyl oxime, ketone, oxime, aldonitrone and ketonitrone. Separations were in most cases sharp, except in the case of the nitrone tautomers, which usually showed some overlapping. When melting points were ambiguous or

low, infrared spectra were used to establish identity or approximate purity. A typical experiment is shown in Table VII. The other essential information appears in Tables I–VI.

In a control analysis, a synthetic mixture of 304 mg. of benzophenone O-benzyloxime, 57 mg. of benzophenone N-benzyloxime and 57 mg. of benzaldehyde N-benzhydryloxime was treated in the foregoing manner. There were recovered 301, 57 and 52 mg., respectively; total recovery 98%.

Alkyl Oximes.—When sufficient O- or N-alkyl oxime was obtained from the chromatographic analyses, it was purified by recrystallization and characterized by melting point, analysis if previously unreported, infrared[33] spectrum (Nujol mull), and, for one of each pair of nitrones, hydrolysis. This information is summarized in Table VIII.

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(33) A Perkin–Elmer model 21 instrument was used.

Selective Hydrocracking of C9- to C12-Alkylcyclohexanes on Acidic Catalysts. Evidence for the Paring Reaction[1]

BY CLARK J. EGAN, G. E. LANGLOIS AND R. J. WHITE

With a nickel sulfide on silica–alumina or with a silica–alumina catalyst below about 300–350°, a C_{10}–C_{12} alkylcyclohexane having n carbon atoms cracks selectively to form principally isobutane and a cycloalkane having n-4 carbon atoms. Structural isomers crack to give the same product distribution by carbon number. Under these cracking conditions, the cycloalkane ring is quite stable. For example, with polymethylcyclohexanes, a reaction occurs that, in its over-all effect, peels or pares methyl groups from the cycloalkane ring and eliminates them as branched alkanes without loss of ring structure. This reaction, which has been named the paring reaction, occurs more readily with cycloalkanes than with monocyclic aromatic hydrocarbons. A mechanism is proposed that involves a rapid isomerization to a common mixture of carbonium ions on the catalyst surface. This is followed by selective cracking at a slower rate of certain carbonium ions that have at least four carbons in a branched side chain.

Introduction

Relatively few papers have been published on the catalytic cracking of cycloalkanes.[2-4] In these papers, either silica–zirconia–alumina or silica–alumina catalyst was used at 500°; no evidence of highly selective cracking reactions was reported. Similarly, relatively few papers have been published on the hydrocracking of cycloalkanes. Gault and Germain[5] report non-selective conversions of tri- and tetramethylcyclopentanes over a platinum–alumina catalyst at 300–350° in the presence of hydrogen. In contrast, the hydroisomerization of cycloalkanes over dual functional catalysts, such as nickel–silica–alumina, has been studied extensively as discussed in recent review articles.[6,7]

The unusual product distribution obtained in the hydrocracking of an aromatic hydrocarbon,

hexamethylbenzene, over a nickel sulfide on silica–alumina catalyst was described recently.[8] It was shown that the principal products are lower molecular weight methylbenzenes and branched alkanes, particularly isobutane. A reaction occurs that, in effect, peels or pares methyl groups from the aromatic ring and eliminates them as branched alkanes with essentially no loss of ring structure. This reaction has been named the *paring reaction*.

This paper describes the behavior of alkylcyclohexanes containing at least three carbons in the side chain or side chains under certain hydrocracking conditions. It is shown that a paring reaction occurs with these cycloalkanes. This paring reaction forms lower molecular weight cycloalkanes and branched alkanes, principally isobutane with a high conservation of ring structure.

Experimental

Equipment.—The experiments were performed in a continuous flow, fixed bed, microcatalytic unit. The 6 ml. of catalyst was supported inside a 0.79-cm. i.d. stainless steel tube 85 cm. in length which was surrounded by a heavy walled steel block inside an electrically heated oven. Catalyst temperatures were measured by a chromel–alumel thermocouple located on the reactor wall at the central portion of the catalyst bed. A Celectray controller was used to control the temperature.

Hydrocarbon feed rates were measured by means of a Microfeeder pump (Proportioneers, Inc.). The hydrogen rate was measured by oil displacement in a reservoir. The hydrogen used was more than 99.5 mole per cent. pure.

(1) The term "paring" denotes a cracking reaction wherein the cyclic structure is preserved and wherein the predominant alkane product from cracking is isobutane.

(2) (a) B. S. Greensfelder and H. H. Voge, *Ind. Eng. Chem.*, **37**, 1038 (1945); (b) B. S. Greensfelder, H. H. Voge and G. M. Good, *ibid.*, **37**, 1168 (1945).

(3) N. A. Radzhabli-Seidova, S. I. Khromov, R. M. Gitina, E. S. Balenkova, E. G. Treshchova and B. A. Kazanskii, *J. Gen. Chem. USSR*, **29**, 2212 (1959).

(4) N. A. Radzhabli-Seidova, S. I. Khromov, Ch. Dorzhin, E. S. Balenkova, E. G. Treshchova and B. A. Kazanskii, *ibid.*, **29**, 2219 (1959).

(5) F. G. Gault and J. E. Germain, "Reprints Second International Congress on Catalysis," Section III, 1960, p. 128.

(6) F. E. Condon in Emmett's "Catalysis," Vol. VI, Reinhold Publishing Corp., New York, N. Y., 1958.

(7) H. Pines and N. E. Hoffman in "Advances in Petroleum Chemistry and Refining," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1960.

(8) R. F. Sullivan, C. J. Egan, G. E. Langlois and R. P. Sieg, *J. Am. Chem. Soc.*, **83**, 1156 (1961).

The catalyst (20–28 mesh) consisted of nickel sulfide (5.3% Ni) on commercial silica–alumina (10% alumina). It was prepared by impregnation of the support with a solution of nickel nitrate, followed by drying and calcination in air. The nickel oxide in the catalyst was then reduced with hydrogen at 300°. The nickel was then sulfided by treating the catalyst with 2% H$_2$S in hydrogen.

Chemicals.—Most of the cycloalkanes, with the exception of n-butylcyclohexane and isobutylcyclohexane, were obtained by hydrogenating the corresponding aromatic hydrocarbon in a 300-ml. rocker bomb (Aminco 2-9/16 o.d. micro series) under approximately 200 atm. of hydrogen with a 5% platinum-on-carbon catalyst (Baker C-1813).

1,2,4-Trimethylcyclohexane was obtained by hydrogenating pseudocumene (Phillips 99% pure) at 82°. A mass spectrometric analysis showed no aromatics in the product; n^{20}D 1.4339 before and after treatment with silica gel. A gas chromatographic (G.C.) analysis showed two peaks, 91% and 9%, which can be accounted for by the geometrical isomers.

sec-Butylcyclohexane was obtained by hydrogenating sec-butylbenzene (Phillips 99% pure) at 65°. After silica gel treatment, the product had a n^{20}D of 1.4464 and showed no aromatics by mass spectrometric analysis.

t-Butylcyclohexane was obtained by hydrogenating t-butylbenzene (Phillips 99% pure) at 120°. Mass spectrometric analysis showed no aromatics; n^{20}D 1.4468.

1,2,4,5-Tetramethylcyclohexane was obtained by hydrogenating durene (99% pure) at 121°. A mass spectrometric analysis showed no aromatic hydrocarbons after silica gel treatment (n^{20}D 1.4446). A G.C. analysis showed three peaks measuring 60, 22 and 18% which can be accounted for by the geometrical isomers.

Isobutylcyclohexane (99.9% pure) was obtained from the American Petroleum Institute.[9]

n-Butylcyclohexane was Eastman Kodak Co. white label and was treated with silica gel before use.

1,2-Diethylcyclohexane was obtained by hydrogenating 1,2-diethylbenzene (K and K Laboratories) at 260°. A G.C. analysis showed two major peaks measuring 92.3% which can be accounted for by the geometrical isomers. A mass spectrometric analysis showed that the remaining impurities were other C$_{10}$-cycloalkanes.

Pentamethylcyclohexane was obtained by hydrogenating pentamethylbenzene (Eastman Kodak Co. white label) at 150°. The pentamethylbenzene showed only one peak in a G.C. analysis. The hydrogenated product had a n^{20}D of 1.4582 after treatment with silica gel. A mass spectrometric analysis showed essentially no aromatics after silica gel treatment. A G.C. analysis showed two major peaks of 79 and 13%, and four smaller peaks.

t-Amylcyclohexane was obtained by hydrogenating t-amylbenzene (Eastman Kodak Co. white label) at 150°. This aromatic showed three peaks of 90, 6 and 4% in G.C. analysis. The n^{20}D was 1.4541 after silica gel treatment of the hydrogenated product. Mass spectrometric analysis showed less than 0.2% aromatics. The product contained 90% t-amylcyclohexane, 6% other amylcyclohexanes and 4% other C$_{10}$-cycloalkanes.

Hexamethylcyclohexane was obtained by hydrogenating hexamethylbenzene (Eastman Kodak Co. white label) at 200°. A mass spectrometric analysis showed less than 0.2% of aromatics; n^{20}D 1.4617.

1,4-Diisopropylcyclohexane was obtained by hydrogenating 1,4-diisopropylbenzene, API sample[9] (99.9% pure), at 264°. A G.C. analysis showed one major peak (97.4%) the remaining impurities being other C$_{12}$-cycloalkanes.

Analysis.—Liquid products were analyzed by G.C. using a temperature programed Perkin–Elmer model 154B with a Dow Corning silicone column. The accuracy of the method was confirmed by analysis of known mixtures of pure hydrocarbons.

The composition of gaseous products was determined by mass spectrometric analysis.

Mixtures of cycloalkane isomers were analyzed by selective dehydrogenation over a platinum-on-silica catalyst (at 349° and 2.5 atm. of hydrogen) and identification of the corresponding aromatics by G.C. in a 20M Carbowax column; G.C. peaks were identified by the relative retention

(9) American Petrolum Institute, Standard Samples of Hydrocarbons, Chemical and Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh 13, Pa,
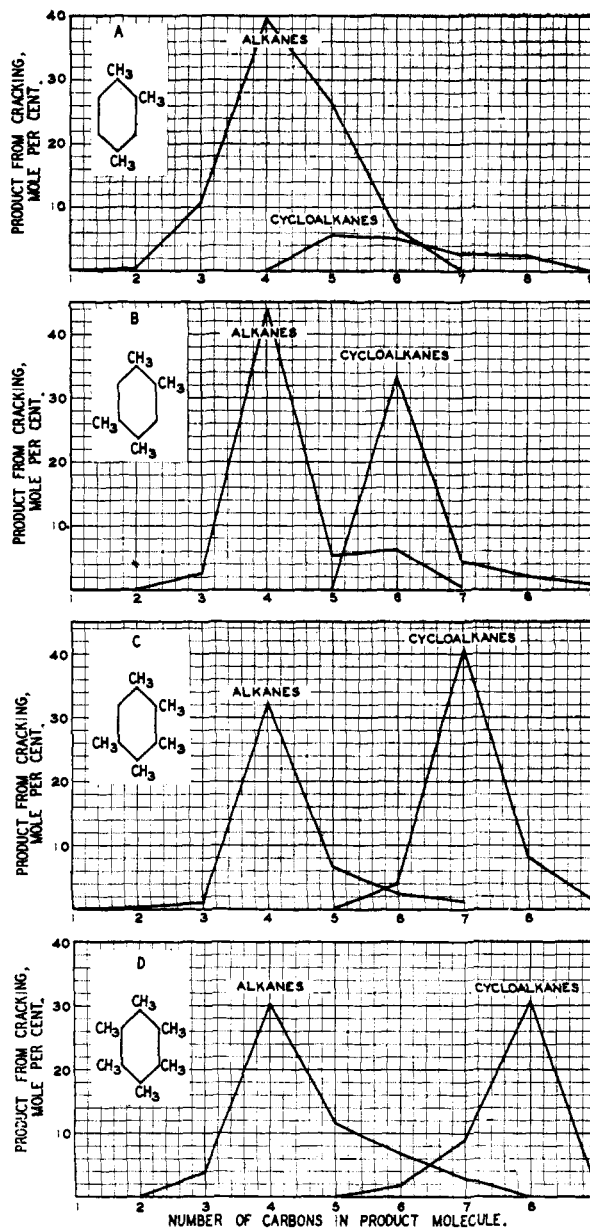

Fig. 1.—Hydrocracking of polymethylcyclohexanes

	Cyclohexane	Conversion to cracking, per cent.	Ring yield, mole %
A	1,2,4-Trimethyl	28.8	32
B	1,2,4,5-Tetramethyl	39.6	81
C	Pentamethyl	27.0	103
D	Hexamethyl	87.5	95

times observed with known mixtures of aromatic hydrocarbons and by mass spectrometric analysis.

Results

I. With Nickel Sulfide on Silica–Alumina Catalyst.—Table I summarizes the experimental conditions and product compositions. Most of the experiments were performed in duplicate.

A. Products from Cracking C$_9$-C$_{12}$-Alkylcyclohexanes. Effect of Molecular Weight.—Figure 1 shows the distribution by carbon number of the products from cracking the cyclohexanes: 1,2,4-

TABLE I

PROCESS CONDITIONS AND PRODUCT COMPOSITIONS

Cyclohexane used	1,2,4-Tri-MCH	1,2,4,5-Tetra-MCH		PMCH	HMCH		n-Butyl	sec-Butyl	Isobutyl	t-Butyl	1,2-Diethyl	t-Amyl	1,4-Diisopropyl	1,2,4,5-Tetra-MCH	
Catalyst	← Nickel sulfide on silica-alumina →													Silica-alumina →	
Expt. no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Temperature, °C.	288	291	348	234	232	288	290	292	286	291	290	234	233	289	344
Pressure, atm.	82	82	82	82	82	82	82	82	82	82	82	82	82	82	82
LHSV[a]	0.1	8.0	8.0	8.0	8.1	8.0	8.0	8.0	8.0	8.0	7.9	8.0	8.0	1.0	8.0
Moles H_2/mole cycloalkane	8.5	8.4	8.4	9.0	9.7	9.9	8.6	8.5	8.6	8.3	8.5	9.0	9.9	7.9	8.5
Residence time, sec.[b]	1104	14.7	13.2	16.4	16.6	14.8	14.6	14.5	14.7	14.6	14.6	16.5	16.3	124.8	13.3
First-order rate constant, sec.$^{-1}$		0.252					0.220	0.255	0.180	0.049	0.097	0.017	0.151		0.165
Rate constant for cracking, sec.$^{-1}$	0.0003	0.034	0.179	0.019	0.125	0.42	0.044	0.058	0.028	0.031	0.033	0.012	0.052	0.002	0.029
Conversion, total, %		97.5					96.0	97.6	92.9	51.1	75.9	24.7	91.5		89.0
Conversion, cracking, %	28.8	39.6	90.5	27.0	87.5	99.8	47.6	57.0	33.9	36.3	38.0	18.1	57.0	19.4	31.9
Product in moles/100 moles of original cycloalkane[c]															
Methane	0.2	0.1	0.1		0.1	0.1									
Ethane	0.1		0.7	0.2	0.2	0.2	0.1	0.1			0.1				
Propane	6.4	1.9	9.6	0.6	1.4	7.8	3.9	6.3	3.6	1.5	3.3	0.3	1.8	1.0	2.4
Isobutane	18.5	33.4	72.5	16.3	59.1	58.7	35.9	37.2	23.4	29.6	26.5	9.6	36.9	16.1	20.5
n-Butane	4.5	0.7	5.8	0.2	1.1	2.3	1.5	1.7	0.8	0.9	2.6	1.2	1.2	0.4	1.0
Isopentane	14.2	4.0	19.2	3.4	21.5	22.8	4.8	5.6	2.6	2.8	4.4	3.9	10.6	2.5	4.8
n-Pentane	1.1	0.2	1.3	0.1	0.2	0.4	0.4	0.3	0.2	0.1	0.2	0.1	0.2	0.1	0.2
Isohexanes	3.6	5.0	18.4	1.2	6.8	13.3	5.9	5.6	3.2	2.5	4.0	0.5	2.2	2.1	4.2
n-Hexane	0.1	0.1	1.1	0.1	0.1	0.2	0.2	0.2	0.1	0.2	0.2			0.1	0.1
Isoheptanes	0.1	0.4	1.1	0.7	4.1	6.2	0.2	0.3	0.2		1.9	0.4	0.6	0.1	0.3
Cyclopentane	3.3														
Methylcyclopentane	2.6	24.5	31.1	2.0	3.1	3.6	27.3	38.7	20.5	22.3	20.3	2.8	1.9	12.1	12.9
Cyclohexane	0.5	1.7	4.1	<0.2	<0.2	<0.2	2.2	2.5	1.6	4.5	1.9	0.6		0.6	1.0
Methylcyclohexane	.8	1.9	4.5	7.3	11.9	13.1	3.1	4.6	3.8	1.6	2.6	9.0	7.2[r]	1.0	2.0
Ethylcyclopentane	.1	0.2	1.0			2.1	0.5	0.6	0.5	0.2	0.3	0.6		0.1	0.2
Dimethylcyclopentanes	.6	1.3	4.5	13.2	9.2	8.4	2.4	3.3	2.1	1.2	1.6	3.8	6.9	.8	1.6
Trimethylcyclopentanes		0.3	0.7	1.1	15.4	12.3	0.8	0.3	0.2	0.3	0.6	0.1	6.1	.1	0.6
Dimethylcyclohexanes		.7	1.3	2.6	32.5	31.0	0.4	1.3	.8	1.1	1.5	.6	33.0	.4	1.0
Other C_8-cycloalkanes[n]	1.4	.8	2.7	0.3	8.5	12.9	1.1	0.4	.5	0.8	1.5	.5	1.5	.3	0.7
C_9-Cycloalkanes	71.2	0.6	1.3	.8	1.4	3.8	1.3	1.1	.8	0.9	0.6	.6	1.3	.8	0.7
C_{10}-Cycloalkanes		60.4[d]	9.5	.6	0.2	0.3	52.4[e]	43.0[f]	66.1[g]	63.7[h]	62.0[g]	.5	0.6	80.6[j]	72.1[k]

TABLE I (continued)

Cyclohexane used	1,2,4-Tri-MCH	1,2,4,5-Tetra-MCH	PMCH	HMCH	n-Butyl	sec-Butyl	Isobutyl	t-Butyl	1,2 Diethyl	t-Amyl	1,4-Diiso-propyl	1,2,4,5-Tetra-MCH
C_{11}-Cycloalkanes			73.0	12.5						81.9[j]	43.0[s]	
C_{12}-Cycloalkanes				0.2								
Total moles in prod. from cracking	58.1	77.8	50.7	176.8	199.5	92.0	110.1	64.9	70.5	74.1	35.1	54.2
Ratio of singly branched to unbranched												
Butanes	4	48	82	54	25	24	22	29	33	10	8	21
Pentanes	13	20	54	108	57	12	19	13	28	19	39	24
Hexanes	36	50	12	68	67	30	28	32	13	19		42
C_4 through C_7[p]	6	43	54	65	35	22	22	27	29	11	11	23
Total moles of cyclo-alkanes in product	80.5	92.4	100.9	94.7	87.7	91.5	95.8	96.6	96.6	92.9	101.0	92.8
Ring yield, %[m]	32	81	103	94	88	82	92	91	87	81	104	77

[a] Volumes of liquid hydrocarbon per volume of catalyst per hour. [b] Apparent time of hydrocarbon in volume occupied by the catalyst; calculated from LHSV assuming no conversion and the perfect gas law for the vapor and hydrogen. [c] Based on 100% recovery of product. [d] Contains 2.5 of 1,2,4,5-tetra-MCH. [f] Contains 4.0 n-butyl-CH. [g] Contains 4.0 C_{10}-aromatic hydrocarbons. [h] Contains 4.0 C_{10}-aromatic hydrocarbons. [k] Contains 4.0 C_{10}-aromatic hydrocarbons. [n] Contains 2.4 sec-butyl-CH. [o] Contains 7.1 isobutyl-CH. [h] Contains 48.9 t-butyl-CH. [i] Contains 75.3 t-amyl-CH. [j] Contains 2.9 C_{10}-aromatic hydrocarbons. [m] Moles of cycloalkanes in product from cracking divided by moles of cycloalkane that cracked. [p] A mixture of C_6-ring and C_6-ring cycloalkanes. [q] Contains 24.1 1,2-diethylcyclohexane. [r] Contains ethylcyclopentane. [s] Contains 8.5 1,4-diisopropylcyclohexane.

trimethylcyclohexane (1,2,4-tri-MCH), 1,2,4,5-tetramethylcyclohexane (1,2,4,5-tetra-MCH), pentamethylcyclohexane (PMCH) and hexamethylcyclohexane (HMCH).

The high selectivity of the cracking reaction of the last three cyclohexanes is striking. The principal acyclic product is isobutane in each experiment, and the principal cycloalkane product contains four carbons less than the original cycloalkane. Very little ring rupture occurs. The yield of cyclic hydrocarbons from the cracking reaction is in excess of 80 mole per cent. of the cycloalkane reactant (except in the case of 1,2,4-tri-MCH). The small amount of methane in the product indicates that the production of lower molecular weight cycloalkanes is not a simple process of demethanation.

A reaction occurs that, in effect, pares methyl groups from cycloalkane rings and eliminates them as branched alkanes, mainly isobutane, in such a way as to conserve rings. For convenience, we have named this the paring reaction.[8]

The magnitude of this reaction is illustrated graphically in Fig. 2 in which the number of moles of carbon found in the acyclic product (from each
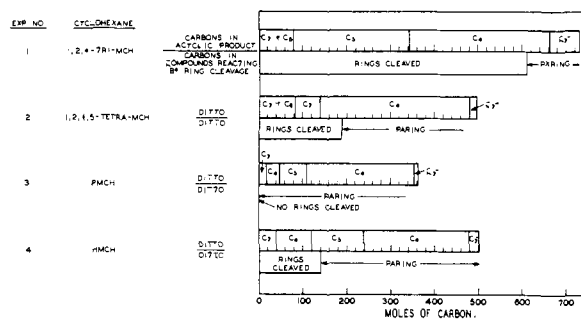
Fig. 2.—Extent of the paring reaction: comparison of moles of carbon in light alkanes produced with moles of carbon in compounds reacting by ring cleavage basis: 100 moles of reactant cracked.

100 moles of original cycloalkane cracked) is compared with the number available from the original cycloalkane that reacted by ring cleavage. From each cycloalkane (except 1,2,4-tri-MCH), there are many more moles of carbon in the acyclic product than can be accounted for by ring cleavage. The remaining alkanes (namely those not accounted for by ring cleavage) must have been formed from methyl groups removed from the ring compounds that remain.

The selectivity of the cracking reaction to form one acyclic product and one cycloalkane product increases noticeably in going from 1,2,4-tri-MCH to 1,2,4,5-tetra-MCH. With the former, the ring yield is low, there is almost as much pentane formed as butane, and there is no single predominant cycloalkane product. The temperature of the PMCH experiment in Fig. 2 is 55° lower than the other experiments. More ring cleavage would be expected if the temperature had been comparable.

Ratio of Singly Branched to Unbranched Alkanes.—A characteristic of the paring reaction of these cycloalkanes is the exceptionally high ratio of singly branched alkanes to unbranched alkanes in
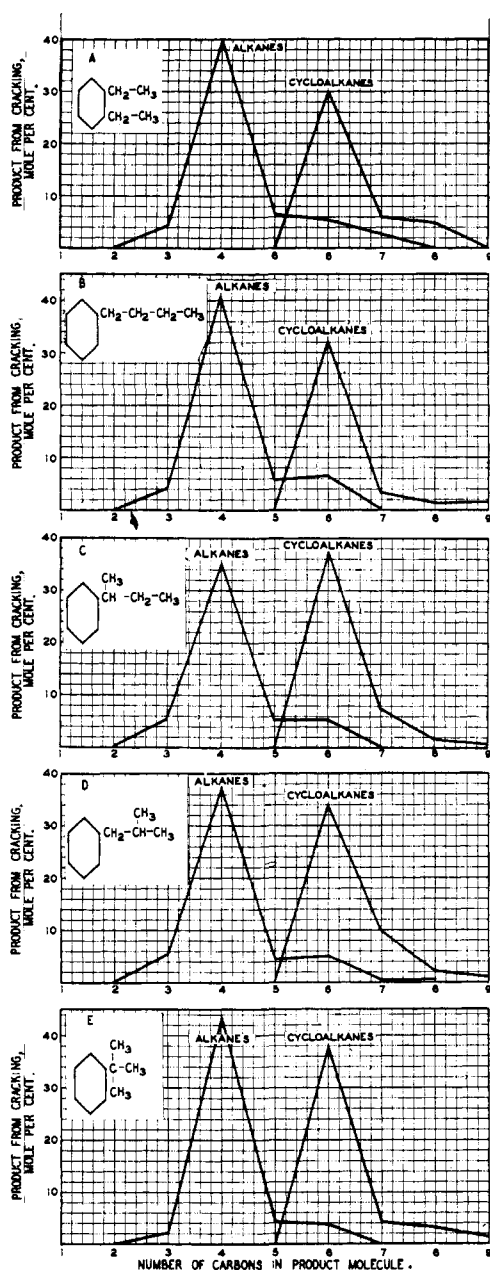
Fig. 3.—Hydrocracking of C_{10}-cyclohexanes at 82 atm., 8.0 L.H.S.V. and 290°.

	Cyclohexane	Conversion to cracked products, %	Ring yield mole %
A	1,2-Diethyl	38.0	81
B	n-Butyl	47.8	82
C	sec-Butyl	57.1	92
D	iso-Butyl	33.9	91
E	t-Butyl	36.4	87

the products. These ratios far exceed the thermodynamic equilibrium ratios as shown in Table II.

Ratio of Cyclopentanes to Cyclohexanes.—The ratio of methylcyclopentane (MCP) to cyclohexane (CH) exceeds the equilibrium ratio by threefold as shown in Table III. In contrast, the differences between the observed and equilibrium ratios with the C_7- and C_8-cycloalkanes are less pronounced.

TABLE II

COMPARISON OF OBSERVED AND EQUILIBRIUM RATIOS OF SINGLY BRANCHED TO UNBRANCHED ALKANES IN THE PRODUCTS

Reactant	Temp., °C.	Alkanes	Ratio Obsd.	Equil.[10]
1,2,4,5-Tetra-MCH	291	Butanes	48	1.1
		Pentanes	20	2.9
PMCH	234	Butanes	82	1.2
		Pentanes	34	3.4
HMCH	288	Butanes	25	1.1
		Pentanes	57	2.9

TABLE III

COMPARISON OF OBSERVED AND EQUILIBRIUM RATIOS OF CYCLOPENTANES TO CYCLOHEXANES IN PRODUCTS

Reactant	Temp., °C.	Carbon no. of cyclo-alkane	Ratio Obsd.	Equil.[11]
1,2,4,5-Tetra-MCH	291	6	14.4	4.6
		7	0.8	1.2
PMCH	234	6	(>10)	3.1
		7	1.8	0.8
HMCH	288	6	(>10)	4.5
		7	0.8	1.2
		8	0.5ᵃ	0.8ᵃ
HMCH	232	6	(>10)	3.1
		7	0.8	0.8
		8	0.5ᵃ	0.6ᵃ

ᵃ Estimated.

Effect of Structure.—Figure 3 shows the distribution of products by carbon number from five isomeric cycloalkanes containing 10 carbons: 1,2-diethyl, n-butyl-CH, s-butyl-CH, isobutyl-CH, and t-butyl-CH. 1,2,4,5-Tetramethyl-CH is shown in Fig. 1B. The similarity of the product distributions is apparent. Again, high ratios of isobutane to n-butane and of MCP to CH are observed. These results show that the composition of the product is essentially independent of the structure of the reactant. The ring yield in each experiment exceeds 80 mole per cent.

The similarity of the product distributions from two isomeric cycloalkanes containing 11 carbons, PMCH and t-amyl-CH, is shown in Fig. 4. The cracking of t-amyl-CH is not a simple dealkylation of a C_5-side chain. Instead, isobutane and C_7-cycloalkanes are the two principal products.

Figure 5 shows the similarity of the product distributions from two C_{12}-cycloalkanes, HMCH and 1,4-diisopropyl-CH. Again, the cracking of the diisopropyl-CH is not a simple dealkylation. Instead, isobutane and C_8-cycloalkanes are the two principal products.

Effect of Temperature.—The paring reaction of the polymethylcyclohexanes becomes more selective at lower temperatures. Evidence for this is: (1) The increased yield of cycloalkanes from cracking. For example, with tetra-MCH (expt. 3 and 2), the yield of cycloalkanes increases from 56 to 81 mole per cent. in lowering the temperature from 348 to 291°. Similarly, with HMCH

(10) E. J. Prosen, K. S. Pitzer and F. D. Rossini, J. Research Natl. Bur. Standards, 34, 403 (1945).

(11) J. F. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer and F. D. Rossini, ibid., 39, 523 (1947).

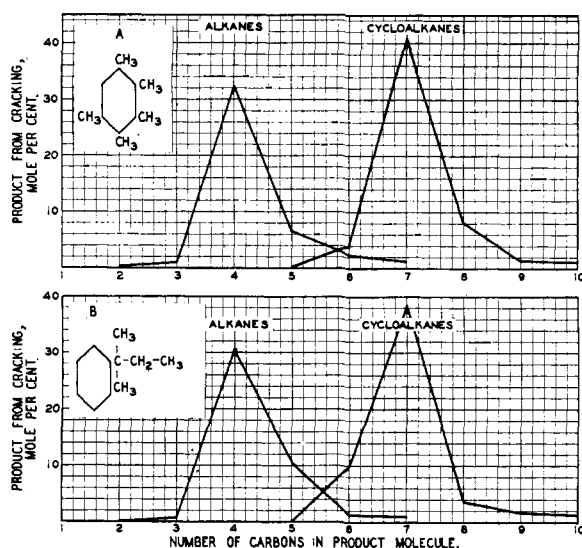Fig. 4.—Hydrocracking of C₁₁-cyclohexanes at 82 atm., 8 L.H.S.V. and 234°C. A, PMCH; B, t-amyl-CH.

Fig. 5.—Hydrocracking of C₁₂-cyclohexanes at 82 atm., 8 L.H.S.V. and 233°C.

(expt. 6 and 5), the yield of cycloalkanes increases from 88 to 94 mole per cent. in going from 288 to 232°. (2) The increased yield of the predominant cycloalkane and alkane species from cracking.

TABLE IV

COMPOSITION OF MIXTURE OF ISOMERS, WEIGHT PER CENT.

Expt. no.	2	9
Temp., °C.	291	286
Cyclohexane used	1,2,4,5-tetra-M	Isobutyl
Amt. unreacted, % of C₁₀-cyclo-		
alkanes in prod.	3.1	9.4
Extent of cracking, %	39.6	33.9
Anal. of mixt., excluding the re-		
actant		
Cyclopentanes	56.5	46.7
Cyclohexanes		
t-Butyl	0.6	
Isobutyl ⎱	0.2	
sec-Butyl ⎰		
1-Methyl-3-isopropyl	1.8	1.9
1-Methyl4-isopropyl	0.8	1.3
1-Methyl-2-isopropyl	0.5	1.1
1,2-Diethyl		
1,3-Diethyl		
1,4-Diethyl		
1-Methyl-3-n-propyl	9.6	12.7
1-Methyl-4-n-propyl		
n-Butyl		
1,3-Dimethyl-5-ethyl	8.4	7.5
1-Methyl-2-n-propyl	1.1	1.3
1,4-Dimethyl-2-ethyl	3.8	4.1
1,3-Dimethyl-4-ethyl	3.6	4.4
1,2-Dimethyl-4-ethyl	6.8	7.6
1,3-Dimethyl-2-ethyl	0.2	0.3
1,2-Dimethyl-3-ethyl	0.9	1.3
1,2,4,5-Tetramethyl		2.8
1,2,3,5-Tetramethyl	4.0	5.4
1,2,3,4-Tetramethyl	1.2	1.6
Cyclohexanes, total	43.5	53.2

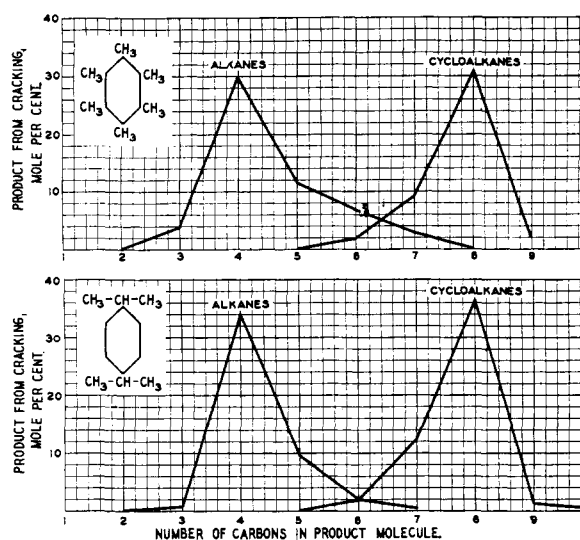For example, with tetra-MCH, 61% of the cycloalkanes is MCP in expt. 3 at 348° as compared to 77% in expt. 2 at 291°.

B. Isomerization Products of C₉- to C₁₂-Alkylcyclohexanes.—A large amount of isomerization occurs in most of the experiments wherein the extent of isomerization could be measured readily. Notable exceptions are the experiments with t-butyl-CH and t-amyl-CH.

Table IV presents the analyses of the C₁₀-cycloalkane isomers formed from tetra-MCH and isobutyl-CH. The similarity of these mixtures of isomers, especially in the relative amounts of cyclohexanes, is striking. These data show that before 40% of the original cycloalkane is cracked, a mixture of isomers is produced that approximates an equilibrium (or a steady state) composition.

C. Rate of Cracking. Effect of Molecular Weight and Temperature.—For correlation of the relative cracking rates, first-order rate constants were calculated from the relationship

$$k = \frac{1}{t} \ln \frac{C_0}{C}$$

Where

k = first-order rate constant for cracking, sec.⁻¹
t = residence time, sec.
C_0 = initial concn. of cycloalkane reactant
C = final concn. of cycloalkane reactant plus isomers

Because of the high conversion in several runs, some of the rate constants are known only approximately.

At 290°, the rate of the cracking reaction increases about 100-fold in going from 1,2,4-tri-MCH to 1,2,4,5-tetra-MCH as shown in Fig. 6. About 87% of the cracking with the C₁₀-cycloalkanes is the paring reaction, wherein isobutane is cracked from the ring. In contrast, with the C₉-cycloalkane, the main reaction is ring opening. In the C₁₀ through C₁₂ carbon number range, the main reaction of the cycloalkanes is the paring reaction; and the rate increases about threefold to fourfold per carbon number. At 233°, the rate increases about sixfold in going from PMCH to HMCH.

Effect of Structure.—The rate constants for cracking of five C₁₀-cycloalkanes at 290° (Table I) shows a maximum spread of a factor of 2. The average rate constant for cracking (and average
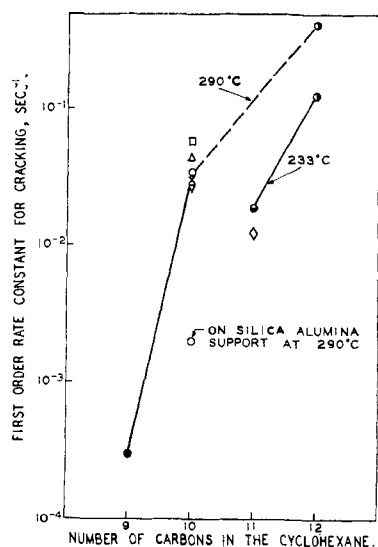
Fig. 6.—Rate constants for cracking on nickel sulfide on silica alumina catalyst: □, sec-butyl-CH; △, n-butyl-CH; O, 1,2,4,5-tetra-MCH; ✕, t-butyl-CH; ▽, iso-butyl-CH; ●, 1,2,4-tri-MCH; ◕, PMCH; ◑, HMCH; ◇, t-amyl-CH.
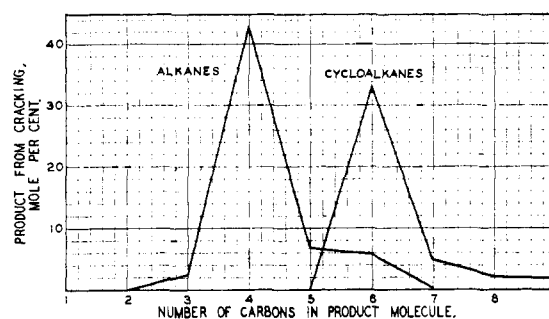

Fig. 7.—Cracking of 1,2,4,5-tetramethylcyclohexane over silica-alumina catalyst. Conditions: 289°C., 82 atm., 1 L.H.S.V.; cracking, 20%; ring yield, 82 mole per cent.
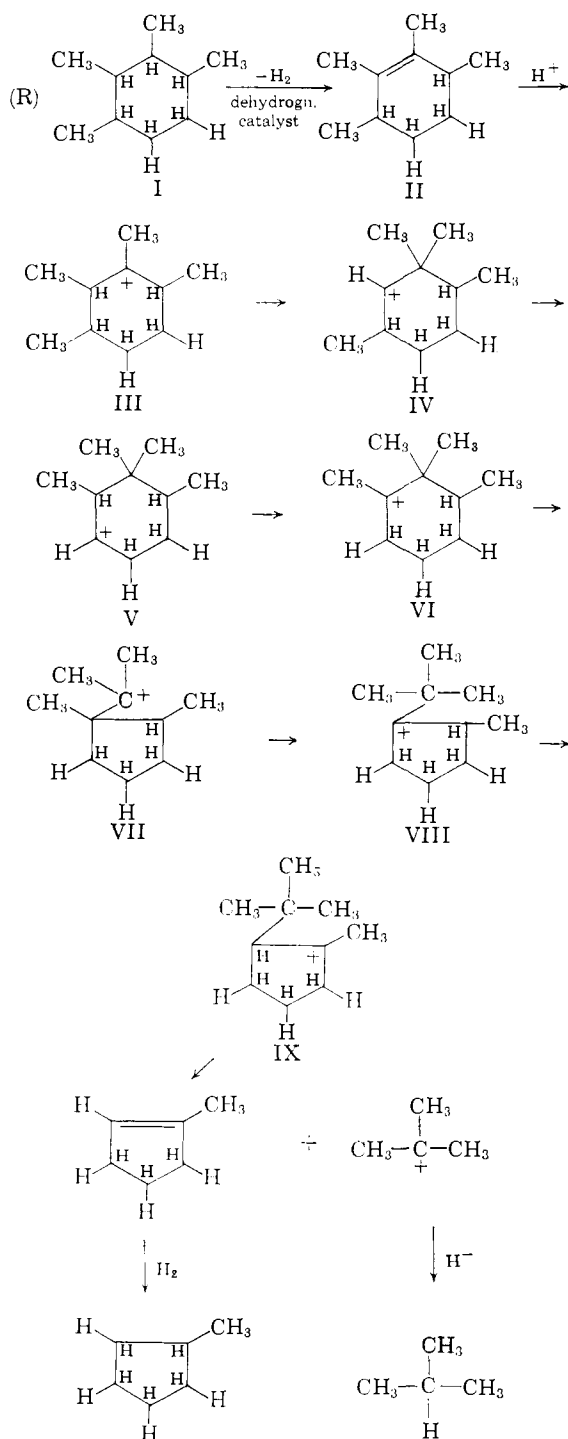
deviation) for these cycloalkanes at 290° is 0.040 ± 0.01. These results suggest that a rapid isomerization step precedes the rate-determining step and that the species that are cracking on the catalyst surface are approximately the same regardless of the structure of the original cycloalkane. The rapid isomerization of C_8-cycloalkanes has been reported.[12]

(D) Rate of Total Reaction.—Approximate rate constants for the over-all reaction are listed in Table I for five C_{10}-cycloalkanes. The rate constant for t-butyl-CH is only one-fourth as large as that for the other isomers. Similarly, t-amyl-CH has a relatively low rate constant for the total reaction as compared to the cracking reaction (0.017 and 0.012 sec.$^{-1}$, respectively).

II. With Silica–Alumina Catalyst.—Polymethylcyclohexanes containing 10–12 carbons undergo the paring reaction on the silica–alumina support alone in the absence of nickel sulfide. Figure 7 shows the product distribution by carbon number for one of the two experiments with 1,2,4,5-tetra-MCH. These products have the characteristic high ratios of branched to unbranched alkanes and of MCP to CH.

Two unusual properties of the products are: (1) the presence of 3–4% of C_{10}-aromatic hydrocarbons and (2) the absence of olefins, such as isobutene. These results can be accounted for by a hydrogen transfer reaction from 1,2,4,5-tetra-MCH to the branched olefins.

The rate of cracking observed with the silica–alumina catalyst is about one-twentieth of that with the nickel sulfide on silica–alumina catalyst at 290° (Fig. 6).

Mechanism

A mechanism for the reactions of these C_{10}–C_{12}-alkylcyclohexanes should account for the following observations: (1) Isomers give the same distri-

bution of products from cracking and crack at about the same rate. (2) The high selectivity in the cracking of the C_{10}–C_{12}-alkylcyclohexanes is not observed with the C_9-alkylcyclohexanes. (3) Isobutane is the principal alkane product in all of the experiments. (4) The ratio of MCP to CH in the products exceeds the equilibrium ratio. (5) High yields of ring compounds are obtained, and very little ring cleavage occurs. (6) Addition of nickel sulfide to the silica–alumina support increases the rate of cracking.

Two papers are pertinent to the mechanisms discussed later: (1) Pines and Shaw[12] have reported the complete scrambling of the carbon atoms in C_8-alkylcyclohexanes (in the presence of a nickel–silica–alumina catalyst at 360°) by a deep seated skeletal rearrangement which involves repeated ring contractions and expansions. (2) Schneider[13] has proposed a mechanism which explains the formation of tetra-MCH's in the alkylation of MCP with isobutene catalyzed by hydrogen fluoride. From an over-all point of view, this reaction is essentially the reverse of the paring reaction of a tetra-MCH. Mechanism R, as shown, is the reverse path of that presented by Schneider.

It is proposed that the first step in the reaction of a cycloalkane having 10 to 12 carbons is a rapid isomerization to a common mixture of carbonium ions on the catalyst surface. This is followed by selective cracking at a slower rate. The product distribution is therefore almost independent of the structure of the original cycloalkane. In the common mixture, a branched side chain of four or more carbons can be formed rapidly by isomerization that involves changes in ring size on the acid sites of the catalyst. This branched side chain on certain carbonium ions described below then cracks, and a lower molecular weight cycloalkane and isobutane (with some isopentane and isohexane, depending on the number of carbons in the original cycloalkane) are formed.

The high selectivity observed suggests that because of the relatively low temperatures of the present experiments, the types of carbonium ions that can crack are restricted. The compositions of the products from cracking indicate that (a) the predominant cracking reactions involve tertiary ions that can produce a tertiary ion by β-scission, for example IX and X; and (b) that isomerization

(12) (a) H. Pines and A. W. Shaw, J. Am. Chem. Soc., 79, 1474 (1957); (b) F. G. Ciapetta, Ind. Eng. Chem., 45, 159 (1953).

(13) A. Schneider, J. Am. Chem. Soc., 76, 4938 (1954).

(R)   I   →$\xrightarrow[\text{catalyst}]{\substack{-H_2 \\ \text{dehydrogn.}}}$→   II $\xrightarrow{H^+}$

III   →   IV   →

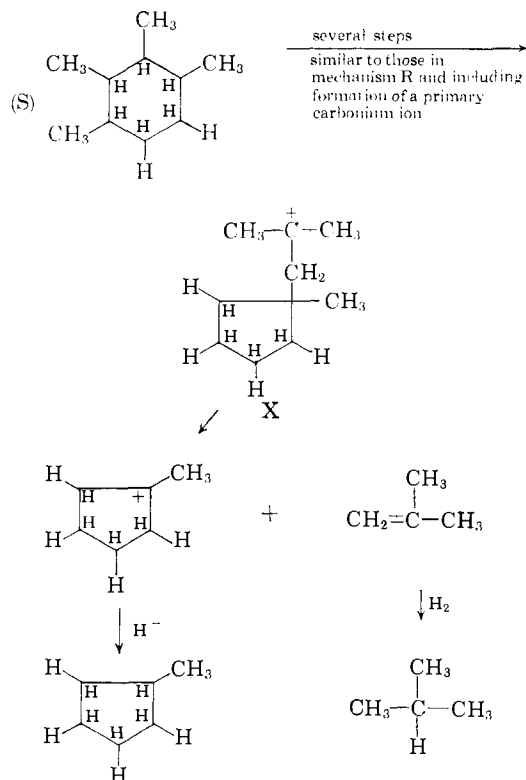V   →   VI   →

VII   →   VIII   →

IX

equilibria of the products from cracking (alkanes or lighter cycloalkanes) are not established, presumably due to rapid displacement from the catalyst surface by the heavier cycloalkane reactants.

Two possible sequences of reactions, wherein tetra-MCH isomerizes to a tertiary ion with a branched side chain of four carbons and then cracks, are shown below. The initial carbonium ions may be formed by: (1) dehydrogenation on the nickel sulfide followed by protonation of the double bond or (2) hydride ion transfer to another carbonium ion.

Mechanism R is characterized by having the positive charge in the ring when cracking occurs, as in IX.

In mechanism S the positive charge is in the side chain when cracking occurs, as in X.

(S) $\xrightarrow[\substack{\text{similar to those in} \\ \text{mechanism R and including} \\ \text{formation of a primary} \\ \text{carbonium ion}}]{\text{several steps}}$

X

After hydrogenation, the products in each mechanism are identical. If tertiary ion to tertiary ion cracking predominates then (a) C$_9$-cycloalkanes do not have a sufficient number of carbons to form the necessary intermediates and, therefore, would not crack with high selectivity, which is in accordance with experimental results; and (b) isobutane rather than propane or n-butane would be formed, which is also in accordance with experimental results.

An explanation of the predominance of C$_4$-alkanes over C$_5$-alkanes is suggested by statistical considerations. For example, in mechanism R, the number of tertiary carbonium ion configurations with a branched side chain of four carbons and an appropriately located positive charge is considerably greater than the number of tertiary carbonium ion configurations with a branched side chain of five carbons and an appropriately located positive charge. With a C$_{11}$-cycloalkane, the nine possible ions with a t-butyl side chain are

cis and trans   cis and trans   cis and trans
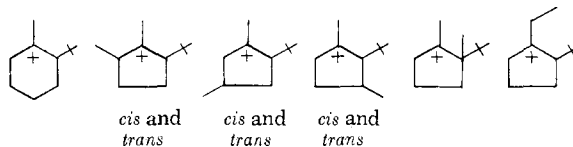
and the single possible ion with a t-amyl side chain is
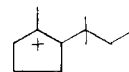
If one assumes each of these species has an equal chance of forming and cracking, then with C_{10}-, C_{11}- and C_{12}-cycloalkanes the ratios of the number of these tertiary ions that produce C_4-alkanes to the number that produce C_5-alkanes are $(1/0 = \infty)$, $(9/1 = 9)$, and $(46/9 = 5.1)$, respectively, for mechanism R, and $(1/0 = \infty)$, $(10/1 = 10)$, and $(56/10 = 5.6)$ for mechanism S. These ratios may be compared to the average observed ratios of isobutane to isopentane of 8.4, 3.6 and 2.7 for C_{10}-, C_{11}- and C_{12}-cycloalkanes, respectively. It is realized that the assumptions of equal concentrations of each of the above species and equal rates of cracking are not valid. Other factors, such as steric effects, will certainly be important; however, these simplified statistical considerations do account qualitatively for the observed relative amounts of C_4- and C_5-alkanes.

From similar considerations, a high ratio of cyclopentanes to cyclohexanes in the products would be expected. This is observed with the C_6-cycloalkanes, especially in the low conversion runs. The data indicate that isomerization equilibrium is being approached more closely at higher temperatures and in higher conversion runs.

An important function of the nickel sulfide in the presence of hydrogen is to maintain catalyst activity by preventing buildup of carbonaceous deposits on the catalyst. Reaction rates are thereby increased. The dehydrogenation activity of the nickel sulfide may also be instrumental in supplying an olefin intermediate for the first step of mechanism R or S. Only the acidic sites of the catalyst are required for the isomerization and cracking; therefore, the paring reaction can occur on the silica–alumina support alone after carbonium ions are once formed.

Stability of the Cycloalkane Ring.—A significant conclusion that can be drawn from this research is that the cycloalkane rings are stable toward ring cleavage under conditions where a branched side chain is easily cracked. At present the reasons for this unusual stability are not completely understood, but the following factors may be important. When ring cleavage of a polyalkylcycloalkane tertiary cation XI occurs, the initial product is a cation containing an olefinic double bond XII.

XI   XII
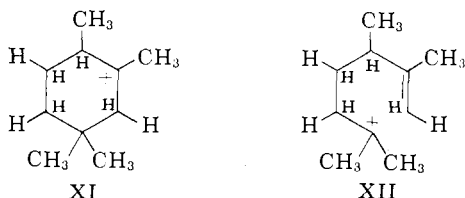
This intermediate is still bound to the catalyst in the activated form. It can, subsequently, (1) hydrogenate to form an alkane of the same carbon number as the reactant, (2) crack again to form lighter acyclic products, or (3) reverse the above reaction and recyclize to form XI or a similar cyclic species. If the last reaction is rapid as compared to the first two, then the concentration of XII will be low and essentially no ring cleavage will

occur. The probability of recyclization is particularly high because the alkene double bond is held in the immediate vicinity of the reactive cationic center by the carbon chain. In the case of the paring reaction (mechanism R or S), on the other hand, the olefinic fragment formed by the cracking reaction is free to diffuse away and be hydrogenated, thus effectively preventing the reverse reaction. It may be, therefore, that bonds in the cycloalkane ring crack about as readily as those in the side chains; but that because of the favorable circumstances for reversing the reaction, the net loss of ring structures is small and the side chain cleavage reaction, which is essentially irreversible, predominates.

Comparison of the Cracking Reactions of Alkyl-cyclohexanes and Alkylbenzenes

The product compositions from the cracking of HMCH and hexamethylbenzene[8] with nickel sulfide on silica–alumina catalyst at 344° differ principally in the carbon number and type of ring compound formed. With HMCH, the principal ring compound is a C_8-cycloalkane. With hexamethylbenzene, the principal ring compound is a C_{10}- or C_{11}-aromatic hydrocarbon. The xylene which is formed first is converted to a C_{10}- or C_{11}-aromatic by a rapid methyl transfer reaction that occurs with polymethylbenzenes but not with polymethylcycloalkanes.

In the hydrocracking of t-amyl-CH with nickel sulfide on silica–alumina catalyst, the predominant acyclic product is isobutane. In striking contrast, isopentane is the principal acyclic product from hydrocracking t-amylbenzene.[14] This difference is a result of the rapid isomerization of the cycloalkane before cracking as contrasted to the aromatic hydrocarbon which cracks the side chain at the ring.

A similar difference exists in the products from n-butyl-CH and n-butylbenzene.[14] The principal alkane is isobutane from n-butyl-CH and is n-butane from n-butylbenzene. These results show that the isomerization of the ring compounds involved in the paring reaction of aromatic hydrocarbons is appreciably slower than the isomerization of the ring compounds involved in the paring reaction of cycloalkanes; hence, the paring reaction does not occur to any appreciable extent with aromatic hydrocarbons if a suitable side chain which can crack rapidly already exists.

The above mechanism of the isomerization of the alkylcyclohexanes can be explained in terms of 1,2-shifts involving classical carbonium ions. In contrast, non-classical ions are probably involved in the isomerization of the corresponding alkylbenzenes.[8]

The hydrocracking of alkanes under these conditions will be described in future publications.

(14) Unpublished results from this Laboratory.