220–225°). The organoborane was slowly distilled. There was obtained 20.7 g. of organoborane, b.p. 186–188°; at 30 mm., evidently tri-*n*-hexylborane. (Tri-*sec*-hexylborane distills at 168–170° at 30 mm.) The product was oxidized. There was obtained 21.8 g. of 1-hexanol, b.p. 155–157° at 743 mm. No 2- or 3-hexanol was detected.

The procedures utilized for the conversion of 2-pentene, 2-octene, the mixed decenes and tetradecenes into the corresponding primary alcohols were identical and need not be described individually. The experimental results are summarized in Table I.

Displacement Reactions of Tri-*n*-pentylborane.—A stock of tri-*n*-pentylborane was prepared by hydroborating 1-pentene.

In a 100-ml. round-bottom flask were placed 20.0 g. of tri-*n*-amylborane (0.09 mole) and 22.2 g. of 1-hexene (0.26 mole). The reaction mixture was heated under reflux for 1 hour under a dry nitrogen atmosphere. The reaction mixture was then fractionated through a Todd column. There was obtained, 17.0 g. of 1-pentene, b.p. 30–31° at 746 mm. The residue distilled through a Vigreux yielded 20.9 g. of tri-*n*-hexylborane, b.p. 124–126° at 1 mm., a yield of 93%.

The procedures were similar in the corresponding reactions involving 1-octene and 1-decene. In the corresponding experiment with 2,4,4-trimethyl-2-pentene, 30.0 g., and tri-*n*-pentylborane, 20.0 g., there was realized only 11.7 g. of 1-pentene after 12 hours of distillation. The residue yielded only 13.9 g. of mixed organoborane with a wide boiling range. The results are summarized in Table II.

Isomerization of 2-octene.—In a 200-ml. round-bottomed flask were placed 50 ml. of triglyme and 40 ml. of 2-octene. The mixture was treated with 15 mmoles of diborane to form a catalytic amount of organoborane. The reaction mixture was heated under reflux for 12 hours (nitrogen) and then slowly fractionated in a Todd column, removing distillate at b.p. 120–121°. There was obtained 22.9 g. of olefin, containing 28% of 1-octene, as indicated by infrared analysis.

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Mechanism of Acid-catalyzed Isomerization of the Hexanes

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A kinetic study was made of the relative rates of interconversion of all the hexane isomers and of the rates of side reactions at different temperatures, at different concentrations of the HF and HF-BF_3 catalysts, and in the presence of inhibitors. A conventional carbonium-ion mechanism accounts for all the facts observed: the need for initiators and a high-dielectric medium, the increase in rate with acidity, the relative rates of conversion of the various isomers, the autocatalytic nature of the cracking reaction, and the change in rates with the concentration of substances that could be carbonium-ion precursors. Cracking inhibitors, such as benzene, were found to function by maintaining the carbonium-ion concentration at a low but constant level and thereby preventing run-away cracking.

The mechanism of the isomerization of alkanes in the presence of a strong acid catalyst has been studied extensively.[1–13] The most favored view is one suggested by Bloch, Pines, and Schmerling[3] and established by Pines and Wackher.[11] They showed that traces of carbonium-ion precursors are necessary to initiate the reaction, and concluded that isomerization proceeds via a chain-carrying, carbonium-ion intermediate. For various reasons, other workers consider a complex between the catalyst and the saturated hydrocarbon as the active intermediate.[5,7,13] Because of these conflicting points of view, additional work to elucidate the mechanism in more detail appeared justified.

In the present study, the relative rates of interconversion of all the hexane isomers and the rates of side reactions were measured at different temperatures, at different catalyst acidities, and in the presence of inhibitors and accelerators. The hexanes were chosen for study because isomerization from a straight-chain configuration to singly and doubly branched forms is possible, side reactions can be controlled, and the products can be analyzed simply. As catalyst, anhydrous hydrogen fluoride promoted by boron trifluoride was chosen because the acidity of this system could be varied over the extremely wide range necessary to measure the widely different rates of isomerization of the methylpentanes and *n*-hexane. Correlations of the rates of isomerization and cracking with the structure of the hydrocarbon and with the other variables could then be expected to shed light on the mechanism of isomerization.

Experimental

The hexanes studied were *n*-hexane, which isomerizes slowly, and 3-methylpentane, which isomerizes much more rapidly. Both were Phillips Petroleum Company technical-grade hydrocarbons. Gas chromatography showed the *n*-hexane to contain about 1% 3-methylpentane and 2.6% methylcyclopentane, and the 3-methylpentane to contain about 0.5% 2-methylpentane. Most of the impurities other than saturated hydrocarbons were removed by extraction with sulfuric acid, percolation through silica gel, and distillation through a short column. *n*-Hexane and 3-methylpentane receiving this treatment were designated "treated feed." For studying the effect of trace impurities, portions of the two hydrocarbons were further purified by shaking for five minutes with aluminum chloride, decanting,

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(1) O. Beeck, Y. W. Otvos, D. P. Stevenson and C. D. Wagner, *J. Chem. Phys.*, **16**, 255 (1948); **17**, 419 (1949).

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(3) H. S. Bloch, H. Pines and L. Schmerling, *ibid.*, **67**, 914 (1945); **68**, 153 (1946).

(4) R. L. Burwell and G. S. Gordon, *ibid.*, **70**, 3128 (1948); **71**, 2325 (1949).

(5) B. L. Evering, E. L. D'Ouville, A. P. Lien, and R. C. Waugh, *Ind. Eng. Chem.*, **45**, 582 (1953).

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(9) A. G. Oblad and M. H. Gorin, THIS JOURNAL, **38**, 822 (1946).

(10) H. Pines, in "Advances in Catalysis," Vol. I, p. 201, edited by Frankenburg, Komarewsky and Rideal, Academic Press, New York, N. Y., 1948; H. Pines and J. M. Mavity, in "The Chemistry of Petroleum Hydrocarbons," Vol. III, Ch. 39, Reinhold Publishing Corp., New York, N. Y., 1955.

(11) H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 595, 1642, 2518 (1946).

(12) F. E. Condon, in "Catalysis," Vol. VI, Ch. 2, Edited by Paul H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1958.

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and then distilling under vacuum into a flask containing sodium. These portions were designated "purified feed."

The boron trifluoride and hydrogen fluoride were commercial grades obtained from Harshaw Chemical Company. The boron trifluoride was used without further purification. The hydrogen fluoride was distilled through a 100-plate Kel-F column into the reaction vessel.

The reactions were carried out in a 250-ml. Hastelloy Magnadash, a magnetically stirred autoclave fitted with a dip-tube for withdrawing samples of the hydrocarbon layer. The autoclave was evacuated and the hydrogen fluoride and boron trifluoride were added. Stirring was started, the contents were brought to reaction temperature, and the hydrocarbon feed was added as rapidly as possible. Samples of the hydrocarbon layer were withdrawn at intervals and analyzed by gas chromatography. At the end of the run, the acid phase was removed and poured onto ice; the liberated "acid-soluble" oil was separated from the aqueous phase, dried, and weighed.

Results

The experiments made with 3-methylpentane were aimed at measuring directly the rates of the three primary isomerization reactions: 3-methylpentane ⇄ 2-methylpentane, methylpentane ⇄ 2,3-dimethylbutane, and methylpentane ⇄ *n*-hexane; at determining the effects of several variables on these rates; and at estimating the rate of the secondary isomerization: 2,3-dimethylbutane ⇄ 2,2-dimethylbutane. The fast reaction to 2-methylpentane and the moderately slow conversion to 2,3-dimethylbutane could both be measured under mild conditions with hydrogen fluoride alone. A stronger acid, HF plus BF_3, was needed for measuring the slow isomerizations to *n*-hexane and 2,2-dimethylbutane. Isomerization to 2,3-dimethylbutane was measurable with both catalysts and thus supplied a link for comparing the rapid interconversion of 2- and 3-methylpentane with the slow conversions to *n*-hexane and 2,2-dimethylbutane.

The experiments made with *n*-hexane were carried out with more boron trifluoride or at higher temperatures in the presence of known cracking inhibitors, benzene and hydrogen. These runs were planned to elicit the effects of catalyst acidity, temperature, and inhibitor concentration on rates of isomerization and cracking.

To permit measurement of the rapid rate of isomerization of 3-methylpentane to 2-methylpentane, the nine experiments reported in Table I were made in HF alone. Five of the experiments were extended to long reaction times in order to measure the rate of the much slower isomerization, methylpentane to 2,3-dimethylbutane.

Table I

Isomerization of Treated 3-Methylpentane with HF at 25°

Time, min.	Catalyst, g./g. feed	Composition of product, % 3-MP	2-MP	2,3-DMB
120	0.23	91	9	0
120	0.53	74	6	0
120	0.87	67	33	0
120	1.35	50	50	0
7000	1.35	32	66	2
14000	1.35	31	66	3
24000	1.35	30	65	5
47000	1.35	29	63	9
78000	1.35	27	59	14

Two other experiments were made under similar conditions with 0.87 g. HF/g. feed to discern the effect of trace impurities. A sample of the purified 3-methylpentane contained only 8% 2-methylpentane after 150 minutes of reaction time. With 0.0001 g. of hexene added per gram of purified feed, the product contained 39% 2-methylpentane after 60 minutes of reaction time. Apparently, purification removed some natural accelerator, the effect of which was restored by adding the trace of hexene.

To permit measure of the slower isomerization rates, experiments were made with a more acidic catalyst, HF plus BF_3. The results are shown in Table II. Rates of all reactions except the rapid interconversion of 2- and 3-methylpentane were measurable. In the series of runs without inhibitor, a small amount of cracking to propane, butanes, and pentanes began to occur after 240 minutes; after 440 minutes, this side reaction became dominant and about 85% of the hexanes disappeared. Cracking was stopped and isomerization was markedly slowed by a conventional inhibitor, as shown by the nine runs with 0.9 wt. % benzene added to the 3-methylpentane feed.

Table II

Isomerization of Treated 3-Methylpentane at 25° with HF-BF_3

(1.5 g. HF and 0.17 g. BF_3 per g. Feed)

	Composition of hexane fraction, %					Other components of product, wt. % of total product	
Time, Min.	3-MP	2-MP	2,2-DMB	2,3-DMB	*n*-Hexane	C_3–C_5 Paraffins	Benzene
			No inhibitor added				
30	27	58	0.6	13	1.5	0.0	0
60	27	57	0.7	14	1.2	0.0	0
90	26	54	1.2	18	1.5	0.0	0
120	27	56	1.6	14	1.7	0.0	0
150	24	50	2.1	21	2.1	0.0	0
195	23	49	2.8	22	2.4	0.0	0
240	24	50	3.3	21	2.7	0.2	0
285	23	48	4.3	22	3.4	0.5	0
325	23	49	6.2	18	4.0	1.3	0
365	22	47	8.9	16	5.6	1.3	0
440	23	48	15.0	8	6.1	4.2	0
485	15	32	32.0	12	8.8	33.0	0
705	8	17	62.0	7	5.5	71[a]	0
			0.9% benzene added to feed				
115	32	61	0.3	6.3	0.4	0	0.7
235	32	57	0.5	9.4	1.3	0	0.7
415	26	52	1.5	18.0	1.5	0	0.6
1005	25	50	3.4	19.0	2.2	0	0.7
1375	24	47	7.4	21.0	4.0	0	0.5
2430	22	44	10.2	19.0	4.6	0	0.4
3870	21	42	13.0	18.0	6.0	0	0.5
5310	20	39	15.0	19.0	7.1	0	0.4
9630	18	36	22.0	16.0	8.5	0	0.4

[a] 14% acid-soluble oil also present.

The runs made on *n*-hexane at 25° also exhibited the "run-away" cracking effect when no inhibitor was used, as shown in Table III. But with 600 p.s.i. hydrogen as inhibitor, both isomerization and cracking stopped. Apparently, hydrogen at this high pressure irreversibly destroys the natural accelerators in the feed.

TABLE III

EFFECT OF HYDROGEN ON ISOMERIZATION OF *n*-HEXANE AT 25°

(0.5 g. HF, 0.5 g. BF_3 per g. *n*-Hexane)

	Composition of hexane fraction, %					Other components, wt. % of total		
Time, min.	*n*-Hexane	2,2-DMB	2,3-DMB	2-MP	3-MP	MCP	CH	C_3–C_5 Paraffins
				No hydrogen present				
75	97	0.2	0.3	1.8	0.9	1.3	1.4	0.0
220	94	0.6	0.8	3.4	1.7	0.2	2.4	0.0
430	90	0.6	2.1	5.0	2.5	0.1	2.5	0.0
770	86	1.2	3.0	6.6	3.3	0.2	2.6	0.2
1425	38	15.0	13.0	23.0	11.0	0.2	2.2	6.5
1535	9	57.0	11.0	17.0	8.0	0.1	1.0	47.5
1615	5	56.0	9.0	21.0	10.0	0.1	0.9	60.0[a]
				With 600 p.s.i. hydrogen				
1020	96	0.1	0.7	2.2	1.0	0.6	2.4	0.0
5340	95	0.2	0.8	2.5	1.4	0.1	2.0	0.0
24360	96	0.1	1.0	2.3	1.1	0.1	2.0	0.0

[a] 20% acid-soluble oil also present.

Experiments at 60° and 83° on treated *n*-hexane with 2.4% added benzene, demonstrated that an increase of 23° increases isomerization rates many fold. They also showed (Fig. 3) that the benzene inhibitor gradually disappears and, after its concentration falls below a critical level, run-away cracking occurs. A similar set of experiments with purified *n*-hexane gave exactly the same results. The similarity between treated and purified feeds at the higher temperatures and boron trifluoride concentrations indicates either that the traces of natural accelerators remaining after purification are enough to start the isomerization reaction and bring it to a steady state, or else that the catalyst itself can abstract a hydride ion from a hexane molecule to produce carbonium-ion initiators.

The effect of lowering catalyst acidity was shown by experiments on *n*-hexane at 83°. With HF plus 10% of its weight of BF_3, the rates of both isomerization and cracking decreased to about one-third the value with HF plus 50 wt. % BF_3.

The effect of 200 p.s.i. hydrogen as inhibitor on conversion of *n*-hexane at 83° was determined. Cracking was almost completely suppressed, and isomerization was about one-sixth as fast as in a parallel run with 2.4% benzene.

Calculation of Rate Constants

In calculating rate constants from the data obtained in these experiments, isomerization was assumed to be a reversible first-order reaction, and the rate expression for the forward reaction, A → B, was defined in a conventional manner

$$dB/dt = k(A_0 - B) - k_{-1}B \qquad (1)$$

But, at equilibrium

$$k_{-1} = k(A_e/B_e) \qquad (2)$$

Upon substitution for k_{-1} in Equation 1 and integration

$$k = \frac{B_e}{(A_e + B_e)t} \ln \frac{A_0B_e}{A_0B_e - (A_e + B_e)B} \qquad (3)$$

where A_0 is the initial concentration of A, A_e and B_e are the concentration of A and B at equilibrium, and B is the concentration of isomer B at time t, in minutes. Rate constants were as calculated for the primary reactions: *n*-hexane to the methylpentanes and the methylpentanes to 2,3-dimethylbutane. The reverse constants were calculated from Equation 2.

This equation cannot be applied directly to the isomerization of 2,3-dimethylbutane to 2,2-dimethylbutane—the second step of a consecutive reaction. However, because the concentration of 2,3-dimethylbutane passes through a broad maximum and is roughly constant over a wide interval of time, an indirect estimation can be made. At this stage, 2,3-dimethylbutane is formed from methylpentane about as fast as it isomerizes to 2,2-dimethylbutane. The net rate of formation of 2,2-dimethylbutane is therefore:

$$\frac{dC}{dt} = kB_c - \frac{B_e}{C_e}kC$$

where C is the concentration of 2,2-dimethylbutane, B_c is the constant concentration of 2,3-dimethylbutane, and B_e and C_e are the equilibrium concentrations of 2,3- and 2,2-dimethylbutane, respectively. Integration of this expression gives

$$k = \frac{C_e}{B_e(t' - t)} \ln \frac{B_c - \frac{B_e}{C_e}C_t}{B_c - \frac{B_e}{C_e}C_{t'}}$$

where C_t and $C_{t'}$ are the concentrations of 2,2-dimethylbutane at times t and t'.

The rate constants calculated for the eight isomerization reactions and one side-reaction—cracking—are summarized in Table IV.

Discussion

An analysis of the results shows that isomerization is initiated and accelerated by such carbonium-ion precursors as olefins, takes place in a high-dielectric medium, and is slowed or stopped by such carbonium-ion traps as benzene or hydrogen. These effects support the conventional carbonium-ion mechanism[2,3,4,11] in which a carbonium-ion is a chain-carrying intermediate. Other observations made on the relative rates of isomerization of the various hexanes and the changes in rates of isomerization and cracking time are also consistent with the carbonium-ion mechanism.

Initiation.—The rate of isomerization depends upon the presence of trace impurities in the feed. The rate constant for the conversion of treated 3-methylpentane to 2-methylpentane was 0.0058 $min.^{-1}$. But, when purified feed was used, the constant dropped to 0.00085 $min.^{-1}$. When 0.01% hexene was added to the purified feed, the rate jumped to 0.01. The isomerization of *n*-hexane in the presence of hydrogen stops completely after a small initial reaction. In contrast, the parallel run without hydrogen shows a sixteen-fold increase in reaction rate. Apparently, the hydrogen gradually saturates the carbonium-ion initiator and stops all reaction:

$$R^+ + H_2 \rightleftharpoons RH + H^+$$

Inhibition by hydrogen indicates that the above reaction proceeds to the right at a finite rate and reaches equilibrium fairly rapidly. The reverse reaction must, therefore, also be fairly fast, and,

TABLE IV

RATE CONSTANTS, k, MIN.$^{-1}$

Experiment				Reaction								
Feed	G. HF/ g. Feed	G. BF$_3$/ g. Feed	Temp., °C.	From: n-C$_6$ To: 2-MP & 3-MP	2-MP & 3-MP n-C$_6$	3-MP 2-MP	2-MP 3-MP	2-MP & 3-MP 2,3-DMB	2,3-DMB 2-MP & 3-MP	2,3-DMB 2,2-DMB	2,2-DMB 2,3-DMB	Hexanes C$_3$–C$_5$
3-MP	0.23	0	25	...	...	0.0008	0.0004	...	...	...	...	...
3-MP	0.53	0	25	...	...	.0027	.0013	...	...	...	...	...
3-MP	0.87	0	25	...	...	.0038	.0019	...	...	...	...	...
3-MP	1.35	0	25	...	...	.0058	.0029	0.000003	...	...	...	...
3-MP^a	1.35	0	25	...	...	.00085	.00042	...	...	...	...	...
3-MP^a and 0.01% Hexene	1.35	0	25	...	...	.01	.005	...	...	...	...	...
3-MP	1.5	0.17	25	0.0012	0.00015	11.6^b	5.8^b	0058	0.020	0.00086	0.00015	0.00003
3-MP and 0.9% Benzene	1.5	.17	25	.0003	.000037	^{c}	^{c}	.00083	.0029	.00027	.00005	.0000002
n-C$_6$^{a}	0.5	.5	25	.00017^d	.000023	^{c}	^{c}	...	^{c}	.00070^e	.00012	...
n-C$_6$ and 2.4% Benzene	1.5	.18	83	.0063	.0013	^{c}	^{c}	^{c}	^{c}	.0072	.0015	.000043
n-C$_6$ and 2.4% Benzene	1.5	.7	60	.004	.00085	^{c}	^{c}	^{c}	^{c}	.0070	.0016	.000012
n-C$_6$ and 2.4% Benzene	1.5	.7	83	.016	.0033	^{c}	^{c}	^{c}	^{c}	.023	.0050	.0001
n-C$_6$ and 200 p.s.i. H$_2$	1.5	.7	83	.0031	.00066	^{c}	^{c}	^{c}	^{c}	.004	.00085	.00001

[a] Purified feed. [b] Estimated from rate in HF alone. [c] Too fast for accurate measurement. [d] Rate constant rose rapidly to more than 0.008 at finish. [e] Rate constant rose rapidly to more than 0.04 at finish.

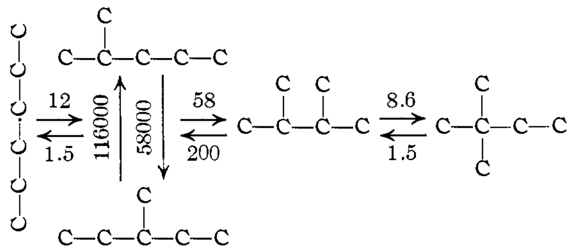
especially at low hydrogen pressures in a strong acid system, could produce significant amounts of carbonium-ion.

Initiation of isomerization, therefore, can proceed not only by the well recognized formation of carbonium ions by reaction with impurities,[11] but also by direct attack of a proton on the paraffin molecule.[8]

Reaction Medium.—The rate of isomerization of 3-methylpentane to 2-methylpentane is approximately proportional to the amount of hydrogen fluoride used. The reaction must, therefore, take place in the body of the acid phase, rather than in the hydrocarbon layer or at the interface. The hydrogen fluoride provides a medium of high dielectric, which facilitates the formation of ionic intermediates.

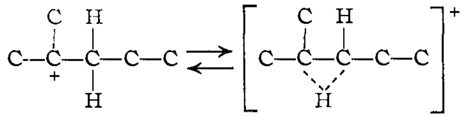
Relative Rates of Isomerization.—Because of the large difference in rates, it was not possible to measure all with the same catalyst. But the rate of isomerization to 2,3-dimethylbutane is 2000 times faster with HF + 10% boron trifluoride than with HF alone. Because all isomerization reactions would probably be affected in the same manner by an increase in catalyst acidity, the rates of interconversion of 2- and 3-methylpentane were assumed to be also 2000 times faster with HF + 10% BF$_3$ than with HF alone. With this assumption, a complete set of values for HF + 10% BF$_3$ at 25° could be calculated. Except for a much higher value for 2- and 3-methylpentane, these relative rate constants agree well with those obtained with HCl-AlCl$_3$ at 100°.[14] The exception may arise because this very fast reaction is limited by mass transfer under vigorous conditions.

The relative rates of isomerization are



A comparison of parallel runs made at 60° and at 83° shows that the absolute rates are about 4 times faster at the higher temperature, but the relative rates change very little.

Isomerization requiring formation of secondary carbonium ions as intermediates in the bimolecular, hydride-ion exchange step are much slower than those involving tertiary carbonium ions.[2] Hence, the rates for conversion to and from n-hexane and to and from 2,2-dimethylbutane are similar and are much slower than the rate of interconversion of 2- and 3-methylpentane. Rearrangement of the tertiary carbonium ion must then proceed by way of cyclic intermediates to avoid formation of a free, secondary carbonium ion[2]



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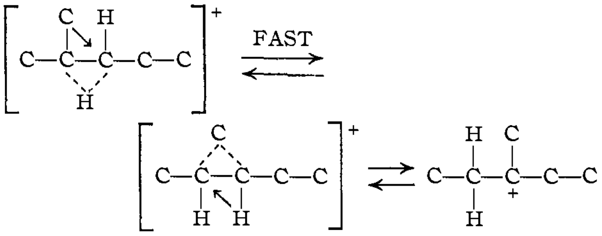
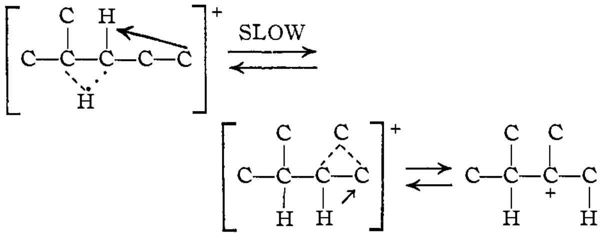
[14] B. L. Evering and R. C. Waugh, *Ind. Eng. Chem.*, **43**, 1820 (1951).

If the 2-methyl group migrates

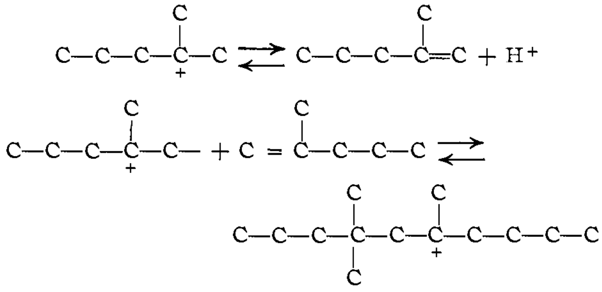


a transition state similar to the above is formed. This transition state can be regarded as pi complex or a resonance hybrid of two secondary carbonium ions. If the methyl group attached to the Number 4 carbon atom migrates

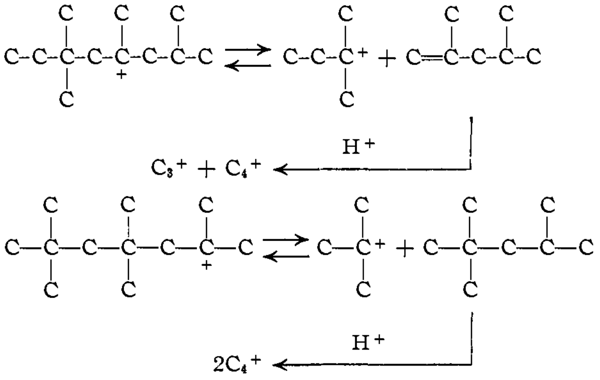


a transition state similar to the above, a resonance hybrid of a secondary and a primary carbonium ion, is formed. Because a much higher activation energy is required to reach the latter transition state, 2-methylpentane will isomerize to 3-methylpentane much faster than it will to 2,3-dimethylbutane. And, in general, isomerizations involving a change in the number of branches in a molecule will be much slower than migrations of an alkyl substituent up and down a straight chain.

Side Reactions.—All series of experiments, except those made under mild conditions with hydrogen fluoride alone, led to continuous formation of propane, butanes and pentanes. Methane and ethane were not detected. This break-down to lighter paraffins must, therefore, be preceded by a dimerization step[15]

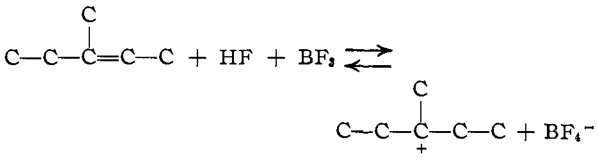


The C_{12} species isomerizes and then breaks down readily by beta fission into C_5, C_4 and C_3 fragments,[16] as shown in the adjoining example, the results of which are in accord with this mechanism.



At constant acidity, conditions that increase the rate of isomerization by raising the carbonium-ion concentration also accelerate cracking at an even faster rate. Thus, isomerization is 3.5 to 4 times as fast at 83° as at 60°, as shown in Table IV, but cracking is about 10 times as fast. Also, the use of 200 p.s.i. hydrogen instead of benzene as a carbonium-ion suppressor reduces the rate of isomerization by a factor of 5; that of cracking, by a factor of 10. Cracking involves addition of a carbonium ion to an olefin as the first step, and the olefin itself is derived from the carbonium ion. Therefore, the rate of cracking is proportional to some power (greater than one) of the C_6 carbonium-ion concentration. Isomerization, on the other hand, is proportional to the first power of the C_6 carbonium-ion concentration. Reduction of the carbonium-ion concentration, therefore, suppresses cracking more than it does isomerization.

Nevertheless, isomerization can be accelerated without changing the relative rate of cracking by increasing the acidity of the catalyst. With HF plus 50% BF_3, isomerization is three times as fast but cracking only 2.5 times as fast as with HF plus 15% BF_3. Increased acidity suppresses the formation of olefins by displacing the following equilibrium toward the right:



$$\mathrm{C{-}C{-}\overset{C}{\overset{|}{C}}{=}C{-}C + HF + BF_3 \rightleftarrows C{-}C{-}\underset{+}{\overset{C}{\overset{|}{C}}}{-}C{-}C + BF_4^-}$$

The C_6 carbonium-ion concentration goes up and thereby increases the rate of isomerization. The olefin concentration goes down and thereby decreases the relative rate of cracking.

Another consequence of the postulated cracking mechanism is that it must be autocatalytic.[5] There is a net increase in carbonium ions when hexanes crack to lighter hydrocarbons. One C_{12} carbonium ion, formed from two C_6 ions, can break down into three C_4 (or $C_5 + C_4 + C_3$) carbonium ions or precursors. The mechanism predicts that cracking, unless checked, continually increases and may become dominant.

Several experiments made with 3-methylpentane and *n*-hexane demonstrate that cracking is autocatalytic, as predicted. Figure 1 illustrates this effect for 3-methylpentane. At the start and for about 400 minutes, isomerization as typified by formation of 2,2-dimethylbutane was steady and cracking to lighter paraffins was slow and even. But then all rates increased rapidly, cracking became a "run-away" reaction, and most of the hexanes disappeared.

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[15] A. Schneider and R. J. Kennedy, THIS JOURNAL, **73**, 5013, 5017, 5024 (1951); **74**, 2553 (1952); L. Schmerling and P. West, *ibid.*, **74**, 2885, 3592 (1952); **75**, 4275 (1953).

[16] F. C. Whitmore and W. A. Mosher, *ibid.*, **63**, 1120 (1941); **68**, 281 (1946).

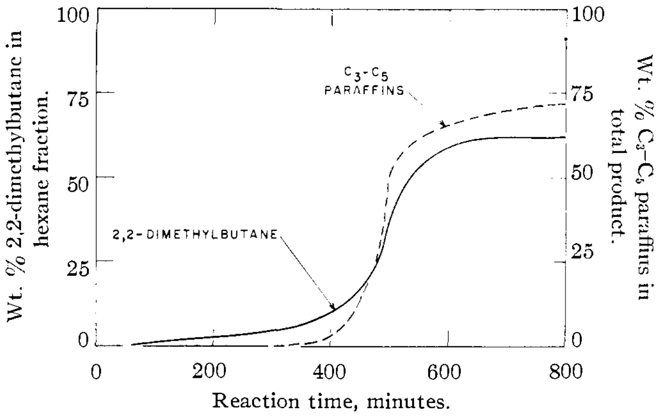


Fig. 1.—Autocatalytic cracking in isomerization of 3-methylpentane.

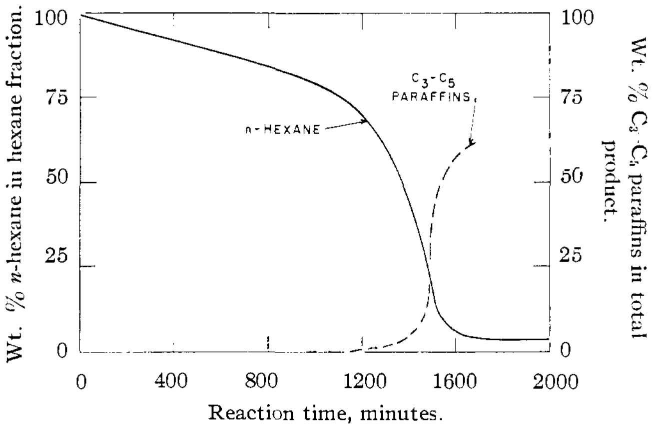


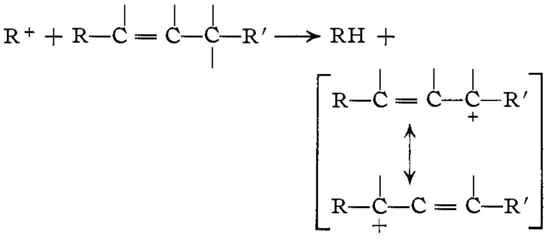
Fig. 2.—Autocatalytic cracking in isomerization of *n*-hexane.

Figure 2 demonstrates that the same is true for *n*-hexane. The rate of isomerization of *n*-hexane holds steady at 0.017% per minute for about 1200 minutes and then increases to more than 0.8% per minute in the next 200 minutes. The rapid increase in rates of both cracking and isomerization is explainable only by the carbonium-ion mechanism.

Another side reaction occurring is the formation of an acid-soluble polyolefinic oil, which accumulates slowly in the catalyst layer. The rate of formation increases rapidly as run-away cracking occurs. About 0.2 g. of oil is produced per gram C_3-C_5 paraffins formed. The oil is highly unsaturated, contains 2 to 3 conjugated double bonds per molecule, has a molecular weight spread from C_{12} to C_{30}, and probably contains one or more C_5 rings per molecule.

Formation of acid-soluble oil, like cracking, probably involves reaction between a carbonium ion and an olefin. But as pointed out by Bartlett, Condon, and Schneider,[17] instead of adding to the olefin, the carbonium ion abstracts a hydride ion from the alpha position and leaves an ion stabilized by allylic resonance, as shown in the equation.

Because this stable carbonium ion cannot abstract a hydride ion from a paraffin, it has a chance to react further by polymerization and hydrogen



$$R^+ + R—\overset{|}{C}=\overset{|}{C}—\underset{|}{\overset{|}{C}}—R' \longrightarrow RH + \left[\begin{array}{c} R—\overset{|}{C}=\overset{|}{C}—\underset{+}{\overset{|}{C}}—R' \\ \updownarrow \\ R—\underset{+}{\overset{|}{C}}—C=\overset{|}{C}—R' \end{array}\right]$$

transfer and is converted into a complicated polyolefinic structure.

Inhibitors.—A comparison of the rate constants shows that the presence of 1% benzene, a conventional inhibitor, in the feed slows down the isomerization reaction by a factor of about 4 and the cracking reaction by a factor of about 100. The runaway cracking reaction is also stopped by the benzene.

The course of the cracking reaction in the presence of benzene is illustrated in Fig. 3. For the first 325 minutes, cracking is constant and under control, and the benzene concentration is gradually decreasing. The carbonium ions are apparently alkylating the benzene to form polyalkylbenzenes, which are basic enough[18] to be taken as protonated complexes into the acid layer. The protonated complexes, bearing a positive charge, are not alkylated by the carbonium ion. There is no net buildup of carbonium ions until the benzene concentration falls below a critical level—about 0.2% under these conditions—and then run-away cracking occurs.

m-Xylene, a basic aromatic that is immediately complexed and taken into the acid layer, was tested and found not an effective inhibitor. Run-away cracking occurred immediately. Hydrogen effectively controls cracking, presumably by hydrogenating the carbonium ion.

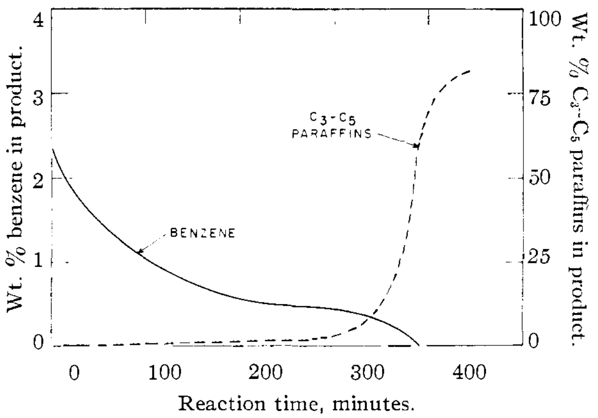


Fig. 3.—Effect of benzene concentration on rate of cracking

A curious effect was noted in the experiments with hydrogen, another conventional inhibitor, at 83°. In the C_4 fraction of the cracked products, the ratio of normal butane to isobutane was about 4 to 1. In all the other experiments either with no inhibitor or with benzene, the ratio was the expected thermodynamic distribution: three parts iso to one part normal. The non-equilibrium distribution

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(17) P. D. Bartlett, F. E. Condon and A. Schneider, This Journal, **66**, 1531 (1944).

(18) D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951).

obtained with hydrogen may indicate that only secondary carbonium ions are active enough to react with hydrogen. Abstraction of a hydride ion from the hydrogen molecule by the secondary carbonium ion leads to the formation of *n*-butane as the primary C_4 product, which then slowly isomerizes to the equilibrium mixture.

Conclusion

A conventional carbonium-ion mechanism accounts for all the facts observed: the need for initiators and a high-dielectric medium, the increase in rate with acidity, the relative rates of conversion of the various isomers, the autocatalytic nature of the cracking reaction, and the change in rates with carbonium-ion concentration. Inhibitors provide a buffer that maintains the carbonium-ion concentration at a low but constant level, and thereby prevents run-away cracking.

The differences in ease of controlling side reactions when isomerizing paraffins other than hexanes are also in accord with this mechanism. A C_5 carbonium ion, when cracked to butane, forms 1.2 new carbonium ions; a C_6 ion gives 1.5 new ions; and a C_7 ion gives 1.75 new ions. Pentanes, hexanes, and heptanes require progressively higher concentration of inhibitors to react with the new carbonium ions as fast as they are formed and thereby prevent a net increase. In the case of heptanes and higher paraffins, it is difficult to add enough inhibitor to control the cracking reaction without stopping isomerization completely. Heptanes and higher paraffins are more susceptible to cracking also because direct breakdown of the heptyl cation to C_4 and C_3 fragments is possible; such breakdown need not be preceded by a dimerization step.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

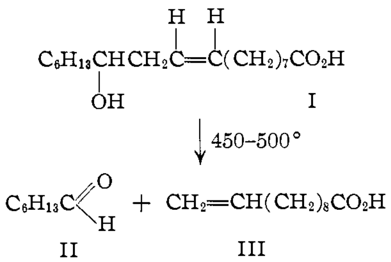
The Pyrolysis of β-Hydroxyolefins

BY RICHARD T. ARNOLD[1] AND GERALD SMOLINSKY[2]

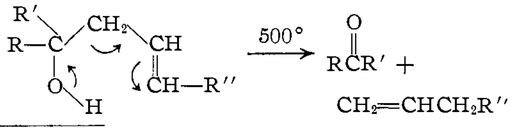
RECEIVED APRIL 13, 1959

In order to examine more fully the manner by which ricinoleic acid undergoes thermal decomposition into heptaldehyde and undecylenic acid, we have prepared a number of related β-hydroxyolefins and subjected these—for short periods of time in a flow system—to temperatures near 500°. The products formed in each case are readily explained in terms of a six-membered cyclic transition state.

Ricinoleic acid (I) and its derivatives form the major fatty acid components of castor oil. The pyrolysis of these substances[3,4] furnishes the most convenient route to heptaldehyde(II) and undecylenic acid(III), and represents one of the most intriguing transformations of a naturally occurring compound.



Several years ago, one of us (R.T.A.)[5] suggested that this decomposition probably occurs *via* a cyclic transition state as illustrated below for the general case.



Although the concept of cyclic transition states has been commonly employed to explain the rearrangements of allylic systems,[6,7] its use has certainly not been restricted to these examples.[8-14] Of especial interest to us is the distinct possibility that the direct formation of unsaturated alcohols from olefins and aldehydes[11,14] is essentially the reverse of the pyrolytic reaction described in this paper.

We have now been able to demonstrate that the thermal decomposition of ricinoleic acid in no way represents a unique situation but is perhaps only the best known example of what appears to be a very general reaction of β-hydroxyolefins.

Specifically, we have prepared the four unsaturated alcohols IV–VII and have shown that each of these substances undergoes a facile conversion at 500° to give quite respectable yields of products anticipated by the proposed mechanism.

An examination of molecular models indicates that the geometric configuration around the carbon–carbon double bond should have no appreciable effect on the course of the reaction. Our experi-

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[1] Alfred P. Sloan Research Associate.

[2] Postdoctorate Research Associate, 1958–1959.

[3] C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Co., Inc. (Reinhold Publ. Corp.), New York, N. Y., 1929, p. 164.

[4] A. A. Vernon and H. K. Ross, THIS JOURNAL, **58**, 2430 (1936).

[5] This proposal was made during a talk before the Organic Division of the American Chemical Society in Boston, Mass., June, 1947.

[6] D. S. Tarbell, *Chem. Revs.*, **27**, 495 (1940).

[7] A. C. Cope and L. Field, THIS JOURNAL, **71**, 1589 (1949), and earlier papers.

[8] F. H. Westheimer and W. A. Jones, *ibid.*, **63**, 3283 (1941).

[9] R. T. Arnold and M. J. Danzig, *ibid.*, **79**, 892 (1957).

[10] R. T. Arnold and J. S. Showell, *ibid.*, **79**, 419 (1957).

[11] R. T. Arnold and J. F. Dowdall, *ibid.*, **70**, 2590 (1948).

[12] W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

[13] C. J. Albisetti, N. G. Fisher, M. J. Hogsed and R. M. Joyce, THIS JOURNAL, **78**, 2637 (1956).

[14] M. Vilkas, G. Dupont and R. Delou, *Bull. soc. chim. France*, 799 (1955).