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Reactions of Hydrocarbons Induced by Alkyl Fluoride–Boron Trifluoride. I. Isomerization of Isoparaffins[1]

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2-Methylpentane, 3-methylpentane, 2,3-dimethylbutane, 2,3-dimethylpentane and 2,4-dimethylpentane were largely isomerized and caused to disproportionate to lower and higher molecular weight isoparaffins in rapid reactions by treatment with 10–15 mole per cent. of isopropyl fluoride in the presence of 5 mole per cent. of boron trifluoride. Both 2,2,4-trimethylpentane and 2,2,5-trimethylhexane underwent disproportionation, but appreciable isomerization was observed with only the latter compound. The isomerizations and their relationship to commercial alkylation of alkanes are discussed in terms of carbonium ions.

Introduction

Acid-catalyzed, heterogeneous, commercial alkylation of alkanes is a process characterized by great complexity of product. Along with isoparaffins of the predicted structure there are produced large numbers of isomeric hydrocarbons of lower and higher as well as of the expected molecular weight.

To explain the presence of isomers of the compounds expected in the product, it has been assumed that the first-formed isoparaffins isomerize under alkylating conditions. In fact, 2-methylpentane and 3-methylpentane[2] and 2,3-dimethylpentane and 2,4-dimethylpentane[3] were interconverted by treatment with 96–97% sulfuric acid; however, these isomerizations required longer times and/or higher temperatures than are employed in commercial alkylation.

The objective of this work was to single out and study the isomerization reaction from the variety of transformations brought about in isoparaffins by systems believed to provide carbonium ions. Isoparaffins of known purity containing dissolved minor amounts of isopropyl fluoride were treated with boron trifluoride. The hydrocarbon products of the reaction were analyzed by fractional distillation and infrared spectroscopy.

Experimental

Materials.—Isopropyl fluoride was prepared according to the method of Grosse and Linn[4] with a minor modification. A liter, stainless steel, pressure reactor fitted with a mechanical stirrer was charged with 208 g. of anhyrous hydrogen fluoride (10.4 moles) and 40 g. of water (2.2 moles). With the temperature maintained at 0° and with vigorous stirring, 180 g. of propylene (4.3 moles) was pressed into the reactor over a period of one hour. The product was removed by evaporation from the acid, passed through a water-scrubbing tower, dried by passage through a potassium carbonate tube, and condensed at −78°. To recover isopropyl fluoride remaining dissolved in the acid, the latter was carefully diluted with 500 cc. of water in the reaction vessel and the liberated gas processed as above. A yield of 237 g. (89%) was obtained boiling from −11 to −10°.

Technical grade, 95 mole % 2-methylpentane ($n^{20}\mathrm{D}$ 1.3715) and 3-methylpentane ($n^{20}\mathrm{D}$ 1.3758) obtained from the Phillips Petroleum Company showed no detectable amount of impurity on analysis by infrared. The 2,3-dimethylbutane used was Phillips "Pure Grade" with $n^{20}\mathrm{D}$ 1.3750. Phillips 95 mole % technical grades of 2,4-dimethylpentane ($n^{20}\mathrm{D}$ 1.3821), 2,3-dimethylpentane ($n^{20}\mathrm{D}$ 1.3914) and 2,2,5-trimethylhexane ($n^{20}\mathrm{D}$ 1.3985) were employed without further purification. Certified isoöctane ($n^{20}\mathrm{D}$ 1.3915) supplied by the Rohm and Haas Company was used without further purification.

Isomerization of 3-Methylpentane (Table I, Expt. No. 1). A Typical Experiment.—The reactions were conducted in a cylindrical copper bomb (21 cm. long by 4.2 cm. in diameter). Into the top were silver-soldered a $^1/_4$" copper entry tube extending to the bottom of the pressure vessel and a take-off tube flush with the top. Both tubes were closed by needle valves.

A solution of 11.3 g. of isopropyl fluoride (0.182 mole) in 100 g. of 3-methylpentane (1.16 moles) was sealed in the bomb and the exit tube was fitted with a pressure gage. Boron trifluoride (3 g., 0.04 mole) was introduced through the entry tube causing the pressure to increase to 70 lb./sq.

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[1] Presented before the Division of Petroleum Chemistry, American Chemical Society, September, 1950.

[2] G. Egloff, G. Hulla and V. I. Komarewski, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1942, p. 41.

[3] P. D. Caesar and A. W. Francis, *Ind. Eng. Chem.*, **33**, 1426 (1941).

[4] A. V. Grosse and C. B. Linn, *J. Org. Chem.*, **3**, 26 (1939).

TABLE I

ISOMERIZATION AND DISPROPORTIONATION OF ISOHEXANES AND ISOHEPTANES INDUCED BY ISOPROPYL FLUORIDE–BORON TRIFLUORIDE

Experiment no.	1	2	3	4	5
Isoparaffin charged	*3-Methylpentane*	*2-Methylpentane*	*2,3-Dimethylbutane*	*2,4-Dimethylpentane*	*2,3-Dimethylpentane*
Temperature, °C.	20–50	20–50	20–40	20–25	20–30
Charge, g. (moles)					
Isoparaffin	100 (1.16)	90 (1.04)	89 (1.03)	83 (0.83)	91 (0.91)
Isopropyl fluoride	11.3(0.182)	9.4(0.15)	11 (0.18)	10 (.16)	9 (.15)
Boron trifluoride	3 (.04)	3 (.04)	3 (.04)	4 (.06)	3 (.04)
Product recovered, wt. % of charge	92	91.0	88.6	92	90
Products, g.^{a} (moles)					
Lower layer	8	6	7	9	4
Gas, (cc.)^c	2 (3.2)	3.4(5.5)	9.3(14.3)	5 (8)	3 (5)
C_5	^{b}	^{b}	1.8(0.03)	^{b}	^{b}
C_6	69.4(0.806)	43.2(0.502)	39.6(.460)	6.7(0.078)	2.9(0.034)
C_7	4.7(.047)	9.1(0.091)	7.7(.077)	36.9(.369)	56.5(.565)
C_8	20.9^d	31.6^d	6.2(.054)	5.0(.046)	1.9(.017)
C_9 and higher			20.1	26.5	24.8
Composition of product,^{e} vol. %					
C_5 Isopentane			2.8		
C_6 2-Methylpentane	38.1	36.3	12.0	3.4	2.2
3-Methylpentane	37.9	18.0	4.1	4.4	...
2,3-Dimethylbutane	...	7.4	39.5	2.4	1.6
C_7 2,4-Dimethylpentane	...	1.1	5.6	32.3	38.2
2,3-Dimethylpentane	...	0.8	3.3	17.3	29.6
2-Methylhexane	3.1	5.2	1.4	2.1	3.4
3-Methylhexane	2.2	4.2	...	2.4	0.8
C_8 2,5-Dimethylhexane			3.7	4.0	1.3
2,4-Dimethylhexane			2.2	2.4	1.1
2,3-Dimethylhexane			2.3	0.6	...
2,3,4-Trimethylpentane			...	0.1	...
C_9 2,2,5-Trimethylhexane			2.9	3.2	0.7
Unidentified compd. below (°C.) vol. %	(118) 1.7	(130) 1.4	(151) 6.8	(145) 4.4	(130)...
Unidentified compd. above (°C.) vol. %	(118) 16.8	(130) 23.5	(151) 14.2	(145) 21.5	(130) 20.6
Distribution of product, wt. %					
Starting isoparaffin	37	33	33	29	27
Isomers	36	24	14	20	38
Lighter and heavier material	27	43	53	51	35
Moles of isoparaffin converted per mole of alkyl fluoride	4.1	4.6	3.8	3.7	4.4

^{a} Calculated in part from distillation data. ^{b} Undetermined. ^{c} Measured at −78°. ^{d} Includes nonanes and higher molecular weight paraffins. ^{e} Infrared analysis.

in. In order to hasten the solution of boron trifluoride in the hydrocarbon, the bomb was shaken once. A marked evolution of heat and a further rise in pressure to 80 lb./sq. in. occurred. After about one minute the heat evolution ceased and the final pressure was 58 lb./sq. in.

The gage was removed, the bomb was cooled to 0°, and there resulted 3.2 cc. of condensed gases when the excess gas was vented through a water-scrubber, dried in a potassium carbonate tube, and condensed in a Dry Ice–acetone trap. A lower liquid layer of 8 g. which fumed strongly in air was separated. The upper layer was saturated to bromine water and weighed 95 g. after washing with water and drying with potassium carbonate. It was distilled in a concentric-tube column rated at about 100 theoretical plates.[5] Five-tenths cc. cuts were analyzed by infrared using a Perkin–Elmer spectrometer. The wave lengths, slit widths and absorption coefficients used are presented in Table II.

A method of successive approximations[6] was used in calculating the composition from the spectrometric data. The accuracy of this method was checked by the analysis of several mixtures of known composition. Agreement between observed and actual concentration for any component was always within 0.5%.

Attempt to Isomerize 2,2,4-Trimethylpentane.—Employing the procedure described above, 0.022 mole of boron trifluoride was added to a solution of 0.18 mole of isopropyl fluoride in 0.78 mole of isoöctane. There was a slight evolution of heat and analysis showed that only 0.29 mole of the isoparaffin was consumed. Approximately 5 vol. % of the product of conversion consisted of rearranged octanes and the remainder boiled above 158°.

Isomerization of 2,2,5-Trimethylhexane.—Addition of 0.029 mole of boron trifluoride to a solution of 0.18 mole of isopropyl fluoride in 0.68 mole of 2,2,5-trimethylhexane at 25° caused the evolution of considerable heat. Infrared analysis on the product could not be performed since hydrocarbon standards in the nonane range were not available. However, fractional distillation showed that little of the original nonane remained and that considerable 2,3,5-trimethylhexane boiling from 128.2 to 130.8° had been formed.

Discussion of Experimental Results

We have found isoparaffins to be unstable in the presence of the system alkyl fluoride–boron trifluoride at temperatures as low as −78°. Boron trifluoride alone has no action on isoparaffins under the conditions employed in these experiments.[7] Whereas alkyl fluorides and boron fluoride[8] are individually soluble in low molecular weight hydrocarbons such as isopentane, a mixture of the three components at 0° immediately reacts and separates into two liquid layers; the weight of the lower layer approximately equals the sum of the weights of the boron trifluoride and of the fluorine in the alkyl fluoride, although this is not intended to imply that the lower layer consists of HBF_4.

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(5) C. K. Donnell and R. M. Kennedy, *Ind. Eng. Chem.*, **42**, 2327 (1950).

(6) J. J. Heigl, M. F. Bell and J. U. White, *Anal. Chem.*, **19**, 293 (1947).

(7) V. N. Ipatieff and A. V. Grosse, THIS JOURNAL, **57**, 1617 (1935).

(8) G. N. Cade, R. E. Dunn and H. J. Hepp, *ibid.*, **68**, 2454 (1946).

TABLE II

WAVE LENGTHS AND BASE-LINE POINTS FOR INFRARED ANALYSIS OF HYDROCARBONS

Compound	Absorption peak	Base-line points		Slit width mm.	Base-line absorbance[a]
2,3-Dimethylbutane	9.64	9.87	9.50	0.235	0.688
2-Methylpentane	13.52	14.07	13.22	.640	.503
3-Methylpentane	10.51	10.75	9.46	.235	.485
2,4-Dimethylpentane	12.34	12.61	11.98	.450	.290
2,3-Dimethylpentane	9.87	10.67	9.50	.235	.324
2-Methylhexane	13.74	14.12	13.22	.640	.477
3-Methylhexane	13.55	14.06	13.23	.640	.383
2,2,4-Trimethylpentane	8.00	8.10	7.87	.190	.630
2,5-Dimethylhexane	10.87	11.10	10.61	.320	.449
2,4-Dimethylhexane	13.04	13.27	12.68	.540	.308
2,3-Dimethylhexane	13.50	13.79	13.22	.640	.218
3,4-Dimethylhexane	10.55	10.83	9.57	.235	.477
2-Methylheptane	13.85	14.07	13.34	.640	.464
4-Methylheptane	13.51	13.80	13.16	.640	.700
3-Methylheptane	10.39	10.62	10.21	.235	.450
2,2,5-Trimethylhexane	8.03	8.15	7.69	.190	.872

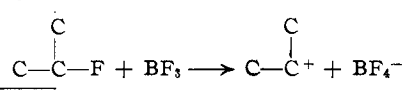
[a] Cell thickness = 0.101 mm.

Isomerization and disproportionation into saturates of lower and higher molecular weights take place simultaneously. Disproportionation is discussed in Paper II of this series.[9] From three to five moles of isoparaffin are converted per mole of alkyl fluoride employed. Treating 10–15 mole % solutions of alkyl fluoride, such as isopropyl fluoride, in isoparaffins with approximately 5 mole % of boron trifluoride, causes isomerization and disproportionation of the hydrocarbons in reactions which are apparently very rapid. Per mole of alkyl fluoride, 0.1 mole of boron trifluoride is more than enough to effect complete conversion of the alkyl fluoride.

Secondary and tertiary alkyl fluorides dissolved in molar excesses of isoparaffins react very rapidly at room temperature with boron trifluoride. Ethyl fluoride has not been thoroughly investigated, but appears to react rapidly under these conditions. Methyl fluoride is inert both at room temperature and 100°.[10]

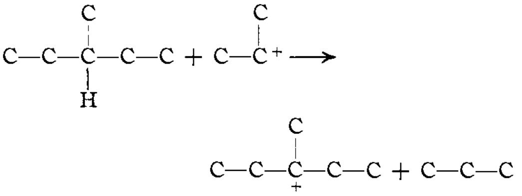
The Isomerization of 3-Methylpentane (Table I, Expt. No. 1).—Acid-catalyzed, aromatic substitution is believed to involve carbonium ion intermediates.[11a] Boron trifluoride, one of the strongest known electron acceptors or Lewis acids,[11b,c] catalyzes a rapid alkylation of toluene by cyclohexyl fluoride.[12] Therefore, boron trifluoride probably produces cyclohexyl carbonium ions rapidly by reaction with cyclohexyl fluoride.

The first reaction caused by adding boron trifluoride to a solution of isopropyl fluoride in 3-methylpentane is therefore probably the ionization of the alkyl fluoride



$$\mathrm{C{-}\overset{C}{C}{-}F + BF_3 \longrightarrow C{-}\overset{C}{C}^{+} + BF_4^{-}} \qquad \text{(I)}$$

As demonstrated by Bartlett, *et al.*,[13] the carbonium ion very rapidly abstracts a tertiary hydrogen, negative ion from the isoparaffinic solvent

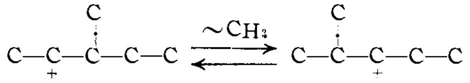


$$\mathrm{C{-}C{-}\underset{H}{\overset{C}{C}}{-}C{-}C + C{-}\overset{C}{C}^{+} \longrightarrow C{-}C{-}\underset{+}{\overset{C}{C}}{-}C{-}C + C{-}C{-}C} \qquad \text{(II)}$$

Here an irreversible reaction takes place, since the propane formed has no tertiary hydrogen atoms to exchange. It has been shown that primary, secondary, and tertiary carbonium ions have no action on normal paraffins under the conditions of this reaction.[10]

The simplest mechanism to explain the isomerization of the 3-methylpentyl to the 2-methylpentyl structure is the two-step process[14a,14b]

$$\mathrm{C{-}C{-}\underset{+}{\overset{C}{C}}{-}C{-}C \overset{\sim H}{\rightleftharpoons} C{-}\underset{+}{C}{-}\overset{C}{C}{-}C{-}C} \qquad \text{(III)}$$



$$\mathrm{C{-}\underset{+}{C}{-}\overset{C}{C}{-}C{-}C \overset{\sim CH_3}{\rightleftharpoons} C{-}\underset{+}{\overset{C}{C}}{-}C{-}C{-}C} \qquad \text{(IV)}$$

The rearranged hexyl ion abstracts a hydride ion from an unrearranged isoparaffin molecule (which is present in much larger concentration), saturates itself, and starts a new cycle.

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[9] A. Schneider and R. M. Kennedy, THIS JOURNAL, **73**, 5017 (1951).

[10] Unpublished results of this Laboratory.

[11a] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 309.

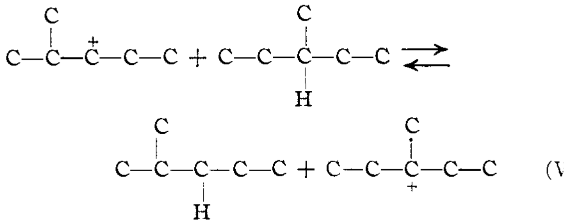
[11b] *Ibid.*, p. 141.

[11c] G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

[12] R. L. Burwell and S. Archer, THIS JOURNAL, **64**, 1032 (1942).

[13] P. D. Bartlett, F. E. Condon and A. Schneider, *ibid.*, **66**, 1531 (1944).

[14] (a) F. C. Whitmore, *ibid.*, **54**, 3274 (1932). (b) Referee II points out that, although there is cogent evidence that highly polar complexes exist in the system under discussion and that various kinds of skeletal isomerizations under such conditions have been cataloged, product distribution in the systems being discussed can hardly betray how the changes in configuration came about. In this paper and those to follow a free ion will frequently be indicated as an intermediate in a reaction. This is not to be interpreted as meaning that the free existence of such ions has been accepted as conclusively proved. This problem is as yet unsolved. Nevertheless, this notation has been conspicuously successful as a means of visualizing mechanisms, correlating results and suggesting new experiments.

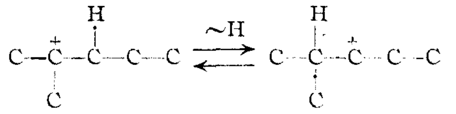


$$\mathrm{C{-}\overset{\overset{C}{|}}{C}{-}\overset{+}{C}{-}C{-}C + C{-}C{-}\underset{\underset{H}{|}}{\overset{\overset{C}{|}}{C}}{-}C{-}C \rightleftarrows C{-}\overset{\overset{C}{|}}{C}{-}\underset{\underset{H}{|}}{C}{-}C{-}C + C{-}C{-}\underset{+}{\overset{\overset{C}{|}}{C}}{-}C{-}C}\qquad \text{(V)}$$

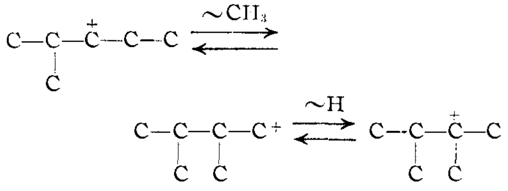
This explains how one molecule of alkyl fluoride can cause the isomerization of many molecules of isoparaffin.

The fundamental process leading to chain termination is loss of a proton from the hexyl ion. The olefin produced is not a chain carrier so that the net effect is a reduction in the concentration of chain initiators in solution. Many interesting phenomena including disproportionation and "self-alkylation" are involved in this reaction and are further discussed in Paper II of the series.[9]

Isomerization of 2-Methylpentane (Table I, Expt. No. 2).—The formation of 2,3-dimethylbutane from 2-methylpentane is explained by the following series of steps:



$$\mathrm{C{-}\underset{\underset{C}{|}}{\overset{+}{C}}{-}\overset{\overset{H}{|}}{C}{-}C{-}C \xrightleftharpoons{\sim H} C{-}\underset{\underset{C}{|}}{\overset{\overset{H}{|}}{C}}{-}\overset{+}{C}{-}C{-}C}\qquad \text{(VI)}$$



$$\mathrm{C{-}\underset{\underset{C}{|}}{C}{-}\overset{+}{C}{-}C{-}C \xrightleftharpoons{\sim CH_3}}$$
$$\mathrm{C{-}\underset{\underset{C}{|}}{C}{-}\underset{\underset{C}{|}}{C}{-}C^{+} \xrightleftharpoons{\sim H} C{-}\underset{\underset{C}{|}}{C}{-}\underset{\underset{C}{|}}{\overset{+}{C}}{-}C}\qquad \text{(VII)}$$

Saturation of the 2,3-dimethylbutyl ion takes place in a manner similar to V. The small amount of 2,3-dimethylbutane formed in the isomerizations of the isohexanes is evidence supporting the hypothesis that the preponderant hexane in isobutane–butylene alkylate, 2,3-dimethylbutane, does *not* derive from the isomerization of other hexanes.

The Isomerization of 2,3-Dimethylbutane (Table I, Expt. No. 3).—This doubly branched hexane undergoes a much more complicated series of reactions than the singly branched hexanes on treatment with isopropyl fluoride and boron trifluoride. Considerably more gaseous product was formed than in the case of the singly branched hexanes.

No neohexane could be detected either by careful fractionation or by infrared analyses. Neohexane is not found to any appreciable extent in alkylations catalyzed by hydrofluoric or sulfuric acids; it is found only when aluminum halide catalysis is employed, and its formation appears to be peculiar to aluminum halides.

The most probable mechanism by which partial unbranching of 2,3-dimethylbutane takes place to form methylpentanes is the reversal of VII.

Inspection of Table I shows that no 2,3-dimethylbutane is produced from 3-methylpentane and only minor quantities from 2-methylpentane. On the other hand, isomerizing 2,3-dimethylbutane gives a product containing 2,3-dimethylbutane, 2-methylpentane and 3-methylpentane in a volume ratio of 3.3:1.0:0.34. The ratio of these compounds occurring in three butene alkylates analyzed by precise fractionation[15] averages 2.9:1.0:0.35. Similarly, in a hydrogen fluoride-catalyzed isobutane–propylene alkylate, the 5 volume % hexane fraction had the distribution 2.1:1.0:0.5 (16). These data are evidence that 2,3-dimethylbutane isomerizing during the alkylation process gives rise to 2- and 3-methylpentane.

Isomerization of 2,4- and 2,3-Dimethylpentane (Table I, Expt. No. 4 and 5).—Isomerization of 2,3-dimethylpentane takes place to such an extent that the product contains more 2,4-dimethylpentane than the starting material. Under the same conditions 2,4-dimethylpentane yields a mixture in which the amount of the 2,4-isomer exceeds that of 2,3-dimethylpentane. The larger amount of disproportionation occurring in the 2,4-dimethylpentane isomerization is discussed in Paper III of this series.[16]

The data on the isomerization experiments of both singly and double branched paraffins demonstrate that, under the conditions of these reactions, retention of the degree of branching of the starting material is preponderant in the products of rearrangements. After the molecule has been converted to the carbonium ion, it is believed that simple migration of a methyl group along the secondary carbon atoms of the molecule is the fastest reaction taking place.

Attempted Isomerization of 2,2,4-Trimethylpentane.—Bartlett, *et al.*,[13] commented on the inertness of isoöctane in the hydrogen–halogen exchange reaction catalyzed by aluminum halide. From the work at hand it appears that somewhat more than one mole of isoöctane was converted per mole of isopropyl fluoride employed. However, the amount of isomerization as a result of this reaction with the isopropyl ion is very small and the major result is "self-alkylation." The inertness of isoöctane to entering into isomerization under these conditions is as yet unexplained.

Isomerization of 2,2,5-Trimethylhexane.—Insertion of another methylene group between the quaternary and tertiary carbon atoms of isoöctane produces a nonane which is exceedingly reactive towards the system isopropyl fluoride–boron fluoride. Steps similar to those postulated by Bartlett[13] for the isomerization of 2,2,4- to 2,3,4-trimethylpentane may be employed to illustrate the rearrangement of 2,2,5- to 2,3,5-trimethylhexane.

NORWOOD, PENNA. RECEIVED SEPTEMBER 29, 1950

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[15] A. R. Glasgow, A. J. Streiff, C. C. Willingham and F. D. Rossini, *Proc. Am. Petroleum Inst.*, **26**, III, 127 (1946).

[16] A. Schneider and R. M. Kennedy, THIS JOURNAL, **73**, 5024 (1951).