[CONTRIBUTION FROM THE RESEARCH LABORATORY, SUN OIL CO.]

Reactions of Hydrocarbons Induced by Alkyl Fluoride–Boron Trifluoride. II. Self-alkylation and Disproportionation of Isoparaffins[1]

BY ABRAHAM SCHNEIDER AND ROBERT M. KENNEDY

The purpose of this work was to study the disproportionation reactions of isoparaffins brought about by systems believed to provide carbonium ions. A marked difference in reactivity between iosbutane and the higher isoparaffins has been observed. Whereas one mole of alkyl fluoride and approximately 5 mole per cent. of boron trifluoride cause the reaction of approximately two moles of isobutane, more than four moles of isopentane are converted under the same conditions. The disproportionation reaction is of secondary importance in treatment of isobutane with the system alkyl fluoride–boron fluoride. Here "self-alkylation" to form trimethylpentanes is the predominant reaction. However, disproportionation is a major reaction in the case of isopentane and higher isoparaffins. Isopentane is converted largely to methylpentanes and isobutane. The degree of branching in the products of disproportionation is essentially the same as that of the starting material. Isopentane and 2-methylpentane give singly branched hexanes, heptanes and octanes. On the other hand, 2,3-dimethylpentane disproportionates largely to 2,3-dimethylbutane and dimethylhexanes. A mechanism is presented which correlates these observations.

Introduction

It has been well established that isoparaffins in contact with systems such as alkyl halides and aluminum halide,[2] secondary or tertiary alcohols and concentrated sulfuric acid,[3] and secondary or tertiary alcohols and concentrated hydrofluoric acid[4] undergo reactions by which they are converted to saturated "self-alkylation" products. This condensation is accompanied by reduction of the alkyl halide or alcohol to the corresponding paraffin.

Marschner and Carmody found that an emulsion of isobutane and concentrated sulfuric acid treated with *t*-amyl alcohol yielded an amount of isopentane equivalent to a large percentage of the alcohol; likewise, isopentane and sulfuric acid caused to react with *t*-butyl alcohol formed isobutane in good yield based on the butanol. Futhermore, consumption of the reagent isobutane and isopentane in each case was about twice as great as could be accounted for by reaction of one mole of isoparaffin per mole of alcohol. Considerable amounts of "abnormal" products were observed—abnormal in that they contained numbers of carbon atoms corresponding to no simple combination of the reagents. In the case of isopentane, *t*-butyl alcohol and sulfuric acid, the depentanized product contained 23 volume per cent. of hexanes and 5 volume per cent. of heptanes.

The same reaction was studied using concentrated hydrofluoric acid, isobutane and *t*-butanol.[4] Here again it was found that, along with the expected octanes, the product contained 10.2 volume per cent. of C_5–C_6 paraffins, 7.3 volume per cent. of C_7 and 4.3 volume per cent. of C_8 hydrocarbons.

The experiments in this paper report part of a study of the low-temperature, acid-catalyzed reactions of isoparaffins. An object of this investigation was to elucidate the nature of processes giving rise to "abnormal" products in commercial alkylation of alkanes promoted by agents other than aluminum halides. To accomplish this, the self-alkylation reaction was studied especially with regard to the identification of the normal and abnormal products. Precise fractional distillation and infrared analysis of the cuts were employed. The system alkyl fluoride–boron fluoride described in Paper I of this series[5] was found to be especially active in effecting self-alkylation and disproportionation of isoparaffins.

Experimental

Materials.—Phillips Petroleum Co. "Pure Grade" isopentane was used without further purification. Phillips 95 mole per cent., technical grade 2-methylpentane (n^{20}D 1.3715) showed no detectable amount of impurity on infrared analysis and was used without further purification. Isobutane (C.P.) and boron trifluoride were those supplied by the Matheson Co.

Isopropyl fluoride was prepared according to the method of Grosse and Linn[6] with the modification described in Paper I of this series.[5] *t*-Butyl fluoride was made according to the directions of Cooper and Hughes.[7]

Technique.—The reactions were conducted in a 600-cc. cylindrical copper bomb (25 cm. long and 6 cm. in diameter) fitted with a 0.25-in. copper entry tube extending to the bottom and a take-off tube leading from the top. Needle valves on each tube were used to seal the bomb. The tared, empty bomb was successively charged with isoparaffin, weighed, pressured to the desired amount with boron fluoride, and weighed again.

A solution of alkyl fluoride in the isoparaffin was then pressured into the bomb through the entry tube ensuring that alkyl fluoride came into contact with boron fluoride dissolved in a large excess of isoparaffin. To permit visual observation and control of the rate of addition of the alkyl fluoride solution, it was added from a high-pressure Jerguson gage-glass connected to the entry tube.

Surprisingly little agitation was required to conduct the reaction. During the addition of the alkyl fluoride, intermittent slight rocking of the bomb was maintained to keep the temperature of the reaction mixture equal to that of the water-bath in which the bomb was immersed. Short times of addition, in the order of ten minutes per half mole of alkyl fluoride, were adequate. Rapid addition was accompanied by a sharp rise in temperature.

The Action of Isopropyl Fluoride on a Solution of Boron Fluoride in Isopentane (Table I, Expt. No. 6), A Typical Experiment.—A 600-cc. bomb charged with 94.5 g. of isopentane (1.31 moles, 150 cc.) and 7 g. of boron fluoride (0.10 mole) was maintained at 22° by immersion in a water-bath. Using the Jerguson gage a solution of 22 g. of isopropyl fluoride (0.36 mole) in 40 g. of isopentane (0.56 mole) was introduced below the surface of the contents of the bomb during a period of ten minutes. The pressure rose from 77 to 103 lb./sq. in.

The bomb was cooled to −78° and the organic phase decanted, separating an upper layer of 144 g. from a lower of 13 g. The organic phase was washed twice with water in a bomb and, to get rid of the last traces of water, was chilled to −78° before being decanted from ice into a stillpot. The

---

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

[2] L. Schmerling, *Ind. Eng. Chem.*, **40**, 2072 (1948).

[3] R. F. Marshner and D. R. Carmody, THIS JOURNAL, **73**, 604 (1951).

[4] J. D. Gibson, R. C. Cole and M. P. Matuszak, *ibid.*, **68**, 2728 (1946).

[5] A. Schneider and R. M. Kennedy, *ibid.*, **73**, 5013 (1951).

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

[7] K. A. Cooper and E. D. Hughes, *J. Chem. Soc.*, 1185 (1937).

TABLE I

SELF-ALKYLATION AND DISPROPORTIONATION OF ISOBUTANE, ISOPENTANE AND ISOHEXANES INDUCED BY ALKYL FLUORIDE–BORON TRIFLUORIDE

Experiment No.	1	2	3	4	5	6	7	8	9
Isoparaffin charged	Isobutane	Isobutane	Isobutane	Isopentane	Isopentane	Isopentane	2-Methylpentane	2-Methylpentane	2-Methylpentane
Alkyl fluoride charged	*t*-Butyl	*t*-Butyl	Isopropyl	Isopropyl	*t*-Butyl	Isopropyl	*t*-Butyl	Isopropyl	Isopropyl
Temperature of bath, °C.	0	29	0	0	0	22	20	27	25
Charge, g. (moles):									
Isoparaffin	120 (2.07)	169 (2.92)	168 (2.90)	124 (1.72)	128.8(1.79)	134.5(1.87)	104.9(1.22)	121.3(1.41)	101.4(1.18)
Alkyl fluoride	22 (0.29)	22 (0.29)	40 (0.65)	19 (0.31)	23.2(0.31)	22 (0.36)	21.1(0.28)	17.7(0.29)	20.6(0.33)
Boron trifluoride	9 (.13)	6 (.09)	6 (.09)	6 (.09)	6 (.09)	7 (.10)	6 (.09)	7 (.10)	7 (.10)
Product recovered, wt. % of charge	83.5	91.5	84	94	86	96	94	90.5	91
Product,^{a} g. (moles):									
Lower layer	10	13	12	10	10	13	16.3	13	15
Propane			^{b}	10 (.23)		7 (0.16)		5 (.11)	14 (.32)
Isobutane	95 (1.64)^{c}	149 (2.56)	113 (1.95)^{c,d}	30 (.52)	40 (.69)	27.8(.48)	1.5(.03)	5.5(.095)	
Isopentane	^{b}	3.7(0.051)	^{b}	31.5(.437)	29.3(.406)	30.2(.419)	9.7(.13)	8.5(.12)	10.5(.145)
C$_6$	1.1(0.13)		3.4(0.039)	18.9(.22)	19.9(.32)	23.1(.268)	47.5(.552)	52 (.60)	18 (.21)
C$_7$	2.5(.025)		7.2(.072)	10.4(.104)	6.4(.064)	11.0(.110)	11.0(.110)	12.5(.125)	12.2(.122)
C$_8$	10.2(.089)		26.0(.23)	10.3(.092)	9.9(.087)	6.0(.053)	10.1(.088)	7.7(.068)	7.1(.062)
C$_9$ and higher	7.2		18.2	19.0	29.0	26	28.1	27.8	39.4
Composition of dependanized product, vol. %^{e}									
C$_6$ 2,3-Dimethylbutane	4.3		5.3	3.4	3.5		5.4		
2-Methylpentane	1.1		1.2	15.7	15.4		38.6	43.4	13.1
3-Methylpentane				8.7	10.0		8.2	16.0	5.5
C$_7$ 2,4-Dimethylpentane	8.5		8.8	2.6	0.7		2.1		
2,3-Dimethylpentane	3.6		4.4	1.7					
2-Methylhexane				5.6	2.8		6.1	7.1	10.7
3-Methylhexane				4.4	3.7		3.5	2.4	4.1
n-Heptane							1.4		
C$_8$ 2,2,4-Trimethylpentane	28.2		18.2		3.2	^{f}	1.0		
2,2,3-Trimethylpentane	2.6		3.6						
2,3,3-Trimethylpentane	6.2		9.1						
2,3,4-Trimethylpentane	3.5		2.7						
2,4-Dimethylhexane	3.0		2.5			0.6			
2,5-Dimethylhexane	3.8		8.2			.7			
2,3-Dimethylhexane	0.6		2.4						
2-Methylheptane						.7		1.4	5.0
3-Methylheptane						1.4		5.7	5.3
4-Methylheptane								0.7	1.1

TABLE I (*Continued*)

C_9 2,2,5-Trimethylhexane	5.0		10.8			7.4			
Unidentified compounds below (°C.), vol. %	(119)0		(125) 0	(92.5) 0	(95.8) 0	(172)21.8	(92) 0	(131.1) 2.0	(121.2) 0
Unidentified compounds above (°C.), vol. %	(119)25.6		(125)22.4	(92.5)57.9	(95.8)60.7	(172)11.2	(92)33.4	(131.1)20.1	(121.2)49.6
Wt. % of isoparaffin charged converted to lighter and heavier material	21.3	12.3[a]	32.7	74.4	77.1	77.6	55.0	57.4	82.1
Moles of isoparaffin converted per mole of alkyl fluoride charged	1.52	1.24	1.46	4.45	4.45	4.03	2.39	2.79	2.94

[a] Calculated in part from distillation data. [b] Undetermined. [c] Removed by refluxing product under ice-condenser, but not fractionated. [d] Contains propane. [e] Infrared analysis. [f] Major part of octane plateau in distillation analyzed to determine Me-heptane content.

mixture was distilled through a partial take-off, total condensation, vacuum-jacketed, silvered column (24" long, $^1/_2$" internal diameter, packed with $^1/_8$" glass helices). Condensation was secured by a trap-like head cooled by a solid carbon dioxide–acetone mixture. Lost in the transfer was 9 g. leaving 135 g. to distil:

−38 to −33°	10 cc. at −80°	7 g. propane
−33 to −14	5 cc.	3 g.
−14 to − 5	37 cc.	24.5 g. isobutane
− 5 to +10	2.5 cc.	1.5 g.
10 to 23	2.5 cc.	1.5 g.
23 to 40	40 cc.	30.5 g. isopentane

The cut boiling from −14 to −5° was analyzed by infrared and found to be at least 95 mole per cent. isobutane.

The head on the column was changed to a water-condenser type and the distillation continued:

40 to 49°	2 cc.	1.5 g.
49 to 70	29 cc.	21.5 g. hexanes
70 to 77	2 cc.	1.5 g.
77 to 100	13 cc.	9.5 g. heptanes
Residue		31 g.

The material boiling above 40° was fractionated in a concentric-tube column and distillate boiling from 118.4 to 127.2° (10.4% of the charge on a no-loss basis) was submitted for infrared analysis with the intent of determining the amounts of the various methylheptanes formed in the reaction.

Discussion of Experimental Results

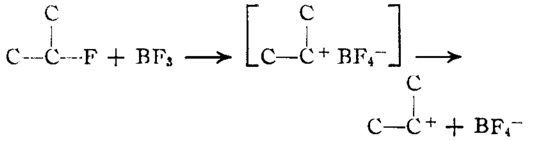
Comparison of the "Self-Alkylation" of Isobutane and Isopentane.—In the experiments involving isobutane (Table I, Expt. No. 1, 2 and 3) between 1.2 and 1.5 moles of isobutane are converted per mole of alkyl fluoride employed. On the other hand, in the experiments with isopentane (Table I, Expt. No. 4, 5 and 6) between 4.0 and 4.5 moles of the isoparaffin are converted per mole of alkyl fluoride used. In both sets of experiments the degree of conversion of isoparaffin appears to be independent of the nature of the alkyl fluoride.

No propane was found in the products of reaction of isobutane with *t*-butyl fluoride and boron trifluoride. Isopentane, however, gave considerable isobutane on treatment with alkyl fluoride and boron trifluoride. From an experiment to determine the quantity of isobutane formed in the disproportionation of isopentane (Table I, Expt. No. 6) it was found that per mole of isopropyl fluoride employed, 4.0 moles of isopentane were consumed and 1.3 moles of isobutane appear.

Only 44% of the expected propane was formed in this experiment. Reaction of all the isopropyl fluoride charged is indicated by its complete absence as shown by infrared analysis of the condensed gases. Thus, apparently a mole of isopropyl fluoride catalyzed the conversion of 4.4 moles of isopentane, whereas the formation of one mole of propane in the exchange reaction caused the conversion of 9.1 moles of isopentane.

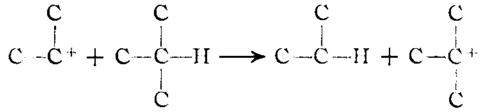
Accompanying the greater reactivity of isopentane over isobutane toward alkyl fluoride and boron trifluoride another difference between the two isoparaffins was found in the nature of the "abnormal" products. Whereas the hexane fraction of isobutane "self-alkylate" was mainly 2,3-dimethylbutane (Table I, Expt. No. 1 and 3) that of the isopentane product was largely 2- and 3-methylpentane (Table I, Expt. No. 4 and 5). In addition, the heptane fractions in the isobutane examples consisted of 2,4- and 2,3-dimethylpentane while those of the isopentane products were composed predominantly of 2- and 3-methylhexane.

The Mechanism of the Self-Alkylation of Isobutane.—As discussed in Paper I of this series,[5] the fastest reaction initiated by boron trifluoride on a solution of isopropyl fluoride in an isoparaffin is most likely the ionization of the alkyl fluoride



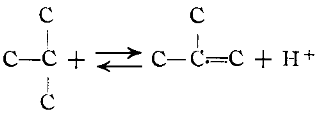
$$\mathrm{C{-}\overset{C}{C}{-}F + BF_3 \longrightarrow \left[C{-}\overset{C}{C}{}^{+}\,BF_4^-\right] \longrightarrow C{-}\overset{C}{C}{}^{+} + BF_4^-} \qquad \mathrm{(I)}$$

Bartlett, *et al.*,[8] demonstrated that a carbonium ion in an isoparaffinic solvent has the ability very rapidly to abstract a hydrogen atom with its pair of bonding electrons from tertiary carbon atoms. The ion is thus reduced to the corresponding paraffin and a molecule of solvent is converted to a tertiary carbonium ion. In isobutane an isopropyl ion is converted to a molecule of propane producing a *t*-butyl ion in an essentially irreversible process



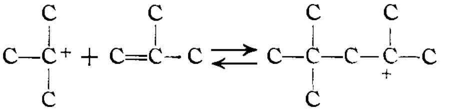
$$\mathrm{C{-}\overset{C}{C}{}^{+} + C{-}\overset{C}{\underset{C}{C}}{-}H \longrightarrow C{-}\overset{C}{C}{-}H + C{-}\overset{C}{\underset{C}{C}}{}^{+}} \qquad \mathrm{(II)}$$

A rapid equilibrium is established between the new ion and isobutylene

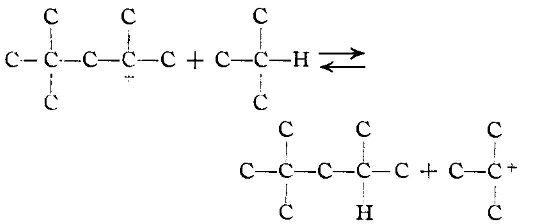


$$\mathrm{C{-}\overset{C}{\underset{C}{C}} + \rightleftarrows C{-}\overset{C}{C}{=}C + H^+} \qquad \mathrm{(III)}$$

From this stage the mechanism developed by Bartlett[8] for aluminum chloride-catalyzed "self-alkylation" of isobutane forming isoöctane is applicable



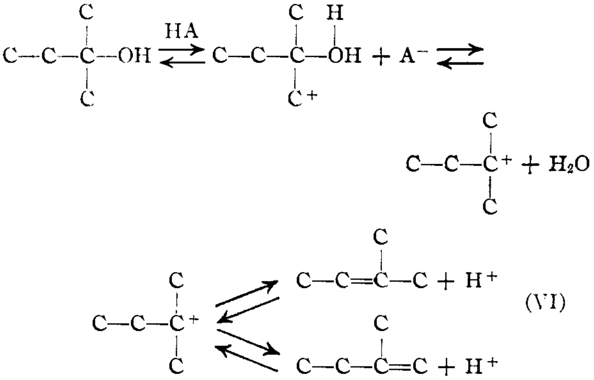
$$\mathrm{C{-}\overset{C}{\underset{C}{C}}{}^{+} + C{=}\overset{C}{C}{-}C \rightleftarrows C{-}\overset{C}{\underset{C}{C}}{-}C{-}\overset{C}{\underset{+}{C}}{-}C} \qquad \mathrm{(IV)}$$



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

The identity and quantity of paraffins formed in the self-alkylation of isobutane depend only to a slight extent on whether isopropyl or *t*-butyl fluoride was employed (Table I, Expt. No. 1 and 3). This indicates that the alkyl fluoride dissolved in large excess of isobutane merely starts cycles of reaction in the solvent. The mechanism of formation of the abnormal products in isobutane–butylene alkylation is discussed in Paper III of this series.[9]

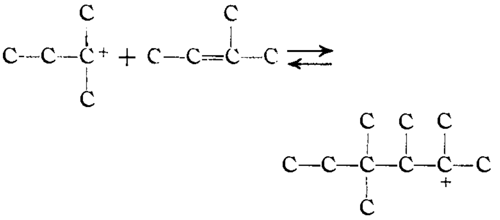
The Disproportionation of Isopentane.—Generation of a carbonium in isopentane as a solvent leads to the formation of the *t*-amyl ion by a reaction analogous to II. This ion may lose a proton either from the secondary or a primary carbon atom to form trimethylethylene or 2-methylbutene-1, respectively. The equilibrium ratio of trimethylethylene to 2-methylbutene-1 formed in acidic dehydration of *t*-amyl alcohol has been shown to be 7 to 1.[10]



$$\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}OH \overset{HA}{\rightleftarrows} C{-}C{-}\overset{C}{\underset{C^+}{C}}{-}\overset{H}{O}H + A^- \rightleftarrows C{-}C{-}\overset{C}{\underset{C}{C}}{}^{+} + H_2O}$$

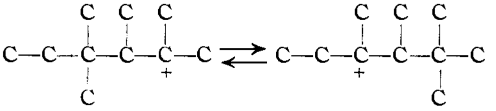
$$\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{}^{+} \rightleftarrows C{-}C{=}\overset{C}{C}{-}C + H^+ ;\quad C{-}C{-}\overset{C}{\underset{C}{C}}{}^{+} \rightleftarrows C{-}C{-}\overset{C}{C}{=}C + H^+} \qquad \mathrm{(VI)}$$

Assuming that trimethylethylene is formed in the preponderant amount in our system, we may write by analogy to IV



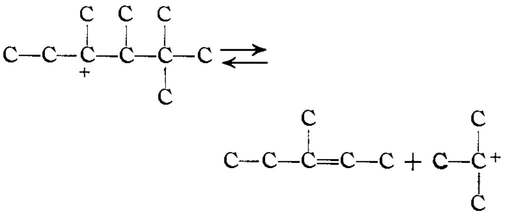
$$\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{}^{+} + C{-}C{=}\overset{C}{C}{-}C \rightleftarrows C{-}C{-}\overset{C}{\underset{C}{C}}{-}\overset{C}{C}{-}\overset{C}{\underset{+}{C}}{-}C} \qquad \mathrm{(VII)}$$

In a study of the acid-catalyzed polymerization of the amylenes Whitmore and Mosher[11] observed that the ion on the right in VII is very unstable toward decomposition into C_5 fragments, *i.e.*, the equilibrium is to the left. Further, it was found that a mobile equilibrium exists involving apparently a "1,3-shift" of a methyl group



$$\mathrm{C{-}C{-}\overset{C}{\underset{C}{C}}{-}\overset{C}{\underset{+}{C}}{-}\overset{C}{C}{-}C \rightleftarrows C{-}C{-}\overset{C}{\underset{+}{C}}{-}\overset{C}{C}{-}\overset{C}{\underset{C}{C}}{-}C} \qquad \mathrm{(VIII)}$$

The ion on the right in VIII cleaves to give a *t*-butyl ion a molecule of 3-methylpentene-2



$$\mathrm{C{-}C{-}\overset{C}{\underset{+}{C}}{-}\overset{C}{C}{-}\overset{C}{\underset{C}{C}}{-}C \rightleftarrows C{-}C{-}\overset{C}{C}{=}C{-}C + C{-}\overset{C}{\underset{C}{C}}{}^{+}} \qquad \mathrm{(IX)}$$

These fragmentation reactions are characteristic of carbon chains containing a quaternary carbon with a positively charged atom two carbons removed from the fully substituted carbon atom. It was observed that no branching on the inter-

---

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

[9] A. Schneider and R. M. Kennedy, *ibid.*, **73**, 5024 (1951).

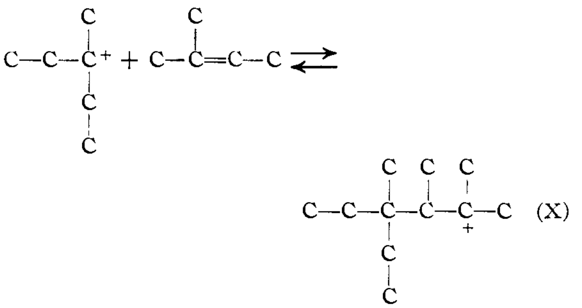
[10] F. C. Whitmore, *et al.*, *ibid.*, **64**, 2970 (1942).

[11] F. C. Whitmore and W. A. Mosher, *ibid.*, **68**, 283 (1946).

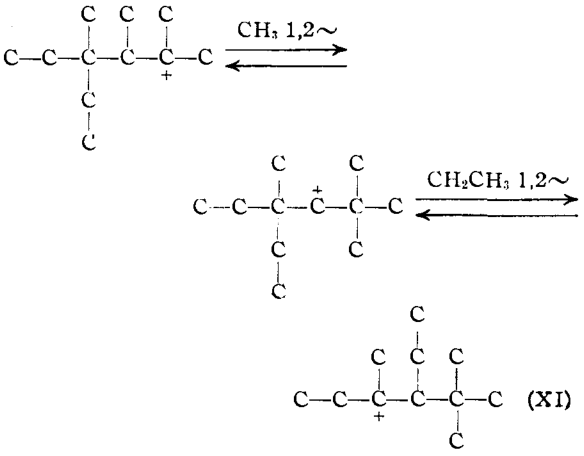
mediate carbon atom makes for difficult cleavage, one branching for ready cleavage, and two for extreme instability.[12]

Applying this mechanism to the system at hand it is seen that IX gives rise to a *t*-butyl ion which reacts with the solvent, isopentane, and is converted to isobutane. The olefinic fragment of IX is saturated by transfer of a proton (such as, for example, from the carbonium ion in VI) forming the 3-methylpentyl ion which may be saturated by a reaction analogous to II with or without prior rearrangement to a 2-methylpentyl ion. Table I, Expt. No. 4, shows the hexane fraction to be a mixture of 2- and 3-methylpentane with the former present in larger amount. This is in accord with the demonstrated ease of isomerization of carbonium ions[5] and with the observed equilibrium constant of 1.96 ± 0.70 for the system 3-methylpentane–2-methylpentane.[13]

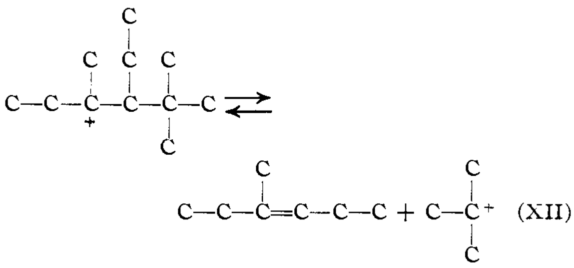
The heptanes recovered from this reaction consist largely of 2- and 3-methylhexane and, to a smaller extent, dimethylpentane. A possible explanation of the formation of singly branched heptanes involves the addition of the *t*-hexyl ion (formed by transfer of a proton to the olefin in IX) to trimethylethylene


(X)

Evidence presented below and in Paper III of this series[9] argues against a direct "1,3-shift" of an alkyl group in the ion on the right of X. "1,2-Shift" of a methyl group adjacent to the carbonium carbon followed by migration of an ethyl negative fragment adequately explains the formation of the observed products



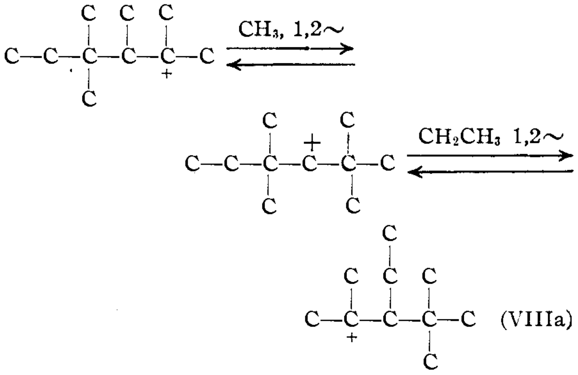
(XI)


(XII)

The olefin is hydrogenated to a mixture of methylhexanes as explained above and the *t*-butyl ion yields isobutane.

The shift of an ethyl group in XI rather than a second methyl migration is inferred because of the complete absence of 3-ethylpentane in the heptane fraction. Confirmatory evidence for the greater migrational aptitude of the ethyl group over methyl is presented in a study of the pinacol rearrangement of 3,4-dimethylhexanediol-3,4 induced by cold, concentrated sulfuric acid.[14] The ketone formed by migration of an ethyl group exceeded by four times the amount formed by shift of a methyl group. Shift of the ethyl group in XI is even more favored by the fact that there are two ethyl substituents to one methyl on the reacting carbon atom.

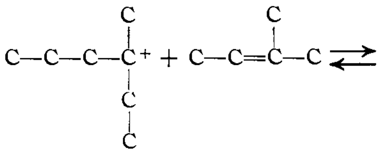
In step VIII the same sequence of rearrangements may be used to arrive at the observed products.



(VIIIa)

Here cleavage of the rearranged ion gives directly the 2-methylpentane carbon skeleton and a *t*-butyl ion. Probably (as illustrated in VIII) two successive methyl rearrangements also take place thus giving ultimately 3-methylpentane and isobutane.

Extending this hypothesis of cleavage of a rearranged, unstable intermediate one step further one would expect, and it is found, that the octane fraction of the product is composed largely of singly branched isoparaffins. The addition of a tertiary 3-methylhexyl ion to trimethylethylene followed by two rearrangements similar to those in XI or VIIIa results in the formation of a molecule of isobutane and one of methylheptane

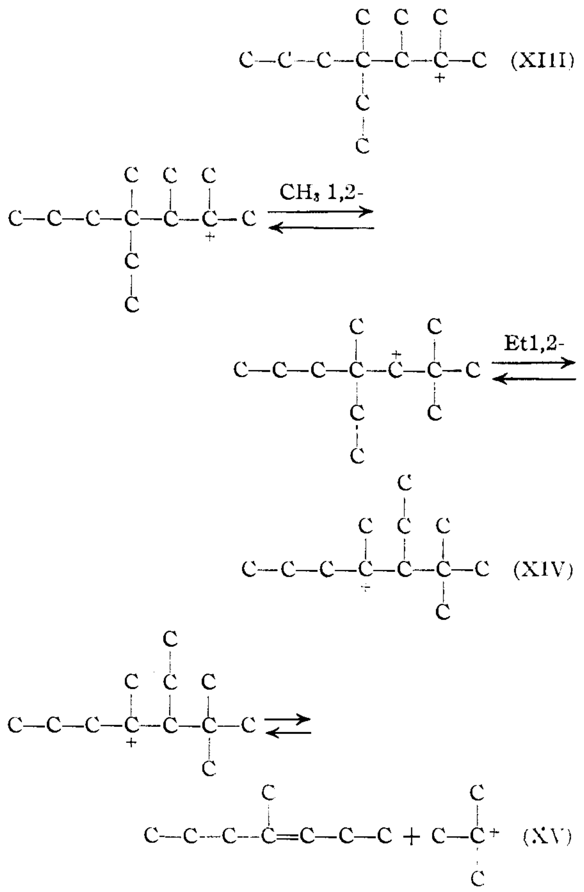


---

[12] F. C. Whitmore and E. E. Stahly, THIS JOURNAL, **67**, 2158 (1945); *ibid.*, **55**, 4153 (1933).

[13] F. D. Rossini, *et al.*, *J. Research Natl. Bur. Standards*, **27**, 540 (1941).

[14] B. Nybergh, *Ber.*, **55**, 1961 (1921).


(XIII)
(XIV)
(XV)

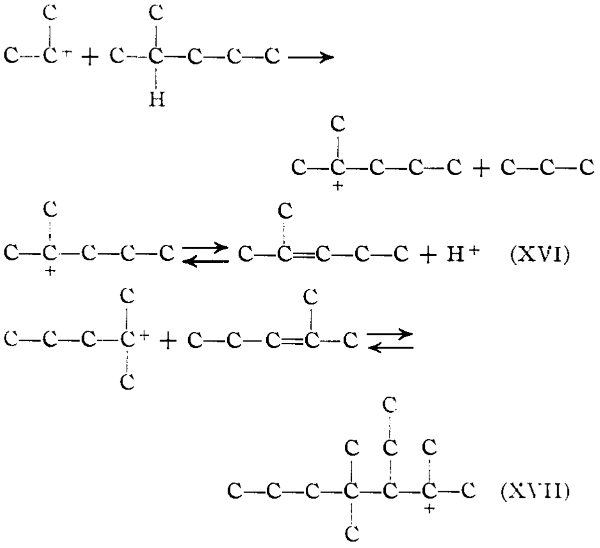
In step XIV the second migration may involve a methyl, ethyl or propyl group; however, the products of all these possible rearrangements are ultimately methylheptanes. Furthermore, addition of a tertiary 2-methylhexyl ion to trimethylethylene in step XIII and the subsequent shifts analogous to those postulated in XIV give rise to singly branched octanes. This illustrates the rule that the degree of branching in the product of disproportionation is largely the same as that of the starting material.

Addition of tertiary carbonium ions to 2-methylbutene-1 and 3-methylbutene-1, the olefins formed in smaller amounts by proton elimination from the *t*-amyl ion, gives a type of adduct resembling the diisobutylene ion, a species long-lived enough to be saturated by abstraction of a hydride ion from the solvent.[5] The decanes, hendecanes, and dodecanes arising thus are "self-alkylates" formed by addition of carbonium ions to olefins both of which are products of disproportionation reactions.

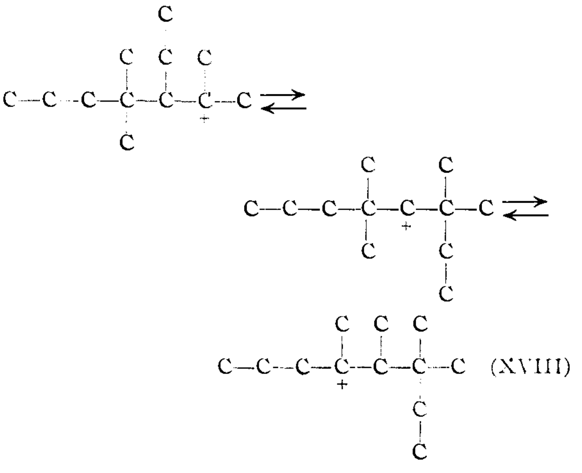
The Disproportionation of 2-Methylpentane.—Table I, Expt. No. 7 shows that per mole of *t*-butyl fluoride employed, 2.4 moles of hexane disappear; per mole of isopropyl fluoride 2.8 moles of the hexane are converted (Expt. No. 8). Little isobutane was recovered in the first case, but the isopropyl fluoride was apparently largely reduced to propane.

There is a rough correspondence in the number of moles of isopentane and heptanes produced in both experiments. Per mole of *t*-butyl fluoride used there were formed 0.47 mole of isopentane and 0.39 mole of heptane (Expt. No. 7); with isopropyl fluoride (Expt. No. 8) the figures are 0.42 and 0.43.

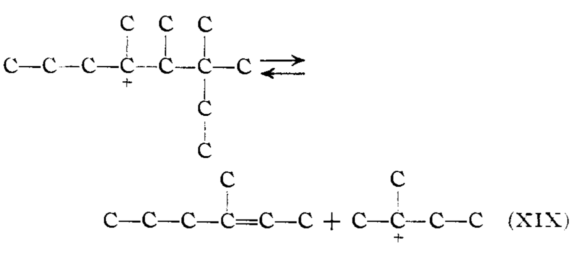
Employing a reaction mechanism similar to that used for the self-alkylation of isopentane we may write


(XVI)
(XVII)

The ethyl group adjacent to the charged carbon migrates leaving a highly unstable pinacolyl type ion[15] which undergoes a practically irreversible rearrangement by shifting a methyl group.


(XVIII)

Cleavage follows yielding 3-methylhexene-2 and a *t*-amyl ion


(XIX)

The olefin and ion are reduced to a mixture of methylhexanes and isopentane, respectively, by the series of reactions described above. Thus, the

---

[15] F. C. Whitmore and F. Johnston, THIS JOURNAL, **60**, 2265 (1938).

number of moles of isopentane and heptane should be equivalent. It is to be expected, however, that the number of moles of isopentane formed should exceed that of the methylhexanes. The former arises in the one-step process of abstraction of a tertiary hydride ion from the solvent molecules by the tertiary amyl ion, while the latter requires transfer of a proton to the methylhexene followed by reduction of the methylhexyl ion. Polymerization, alkylation and disproportionation are reactions which compete with the two-step reduction process to lessen the yield of methylhexanes.

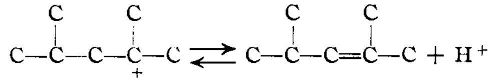
The easy isomerization of 2-methylpentane to 3-methylpentane[5] in the presence of alkyl fluoride and boron fluoride should have no effect in increasing the degree of branching in the heptane fraction. Remembering the discussion on shifting of ethyl radicals it is possible to write four reactions involving the additions of tertiary 2- and 3-methylpentyl ions to 2- and 3-methylpentene-2 giving rise to four C_{12} intermediate ions which, on undergoing the series of rearrangements used in the isopentane example, yield mixtures of 2- and 3-methylhexane and isopentane.

The formation of methylheptanes can be explained by addition of tertiary methylhexyl ions to 2- and 3-methylpentene-2 followed by the two intramolecular rearrangements and cleavages closely paralleling those in steps XVII, XVIII and XIX.

The products from the disproportionation of isopentane and isohexane are thus mostly singly branched molecules. These differ strikingly from the case of isobutane self-alkylation where doubly branched molecules largely make up the "abnormal" products.

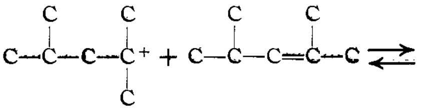
The Disproportionation of 2,4-Dimethylpentane.—An experiment in which the major part of the disproportionation product consisted of doubly branched molecules was the isopropyl fluoride–boron fluoride induced reaction of 2,4-dimethylpentane. It was conducted with the intent of studying the isomerization of a doubly branched paraffin so that a high initial concentration of carbonium ion was provided by introducing boron fluoride into a 12% solution of isopropyl fluoride in the hydrocarbon (Paper I of this series, Table I, Expt. No. 4[5]).

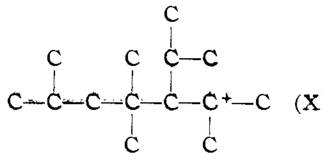
The disproportionation products are again roughly equivalent; 0.08 mole of hexanes and 0.05 mole of octanes were recovered. Applying the mechanism developed for the cases of isopentane and 2-methylpentane one can predict doubly branched products to constitute a major part of the disproportionation product



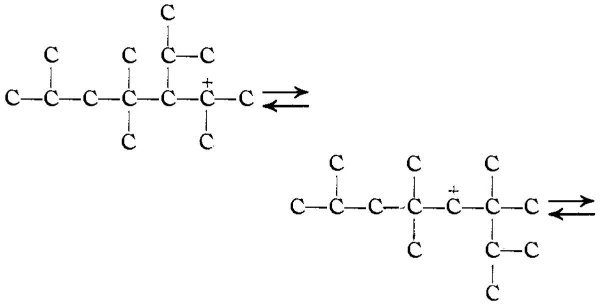
$$C-\overset{C}{C}-C-\underset{+}{\overset{C}{C}}-C \rightleftarrows C-\overset{C}{C}-C=\overset{C}{C}-C + H^+$$

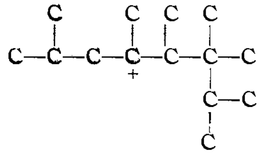
(XX)



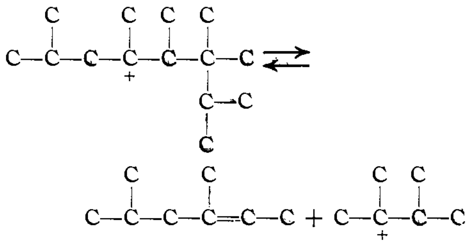


(XXI)





(XXII)



(XXIII)

Step XXII would seem to refute the concept of the direct "1–3 shift." Inspection of the product composition in the above-mentioned table confirms that dimethylhexanes are the major octane components and that the hexane fraction contains a much larger relative percentage of 2,3-dimethylbutane than the cases of either isopentane or 2-methylpentane. This fact has an important bearing on the nature of the origin of the abnormal products in olefin–isoparaffin alkylation to which discussion is given in Paper III of this series.[9]

Discussion of the Apparently Enhanced Reactivity of Isopentane over Isobutane.—If it be assumed that the sole reaction of the octyl ion intermediate in the self-alkylation of isobutane is the formation of isoöctane, then the stoichiometric equation

$$RF + 2C_4H_{10} \longrightarrow C_8H_8 + RH + H^+ + F^-$$

holds; one mole of alkyl fluoride brings about the reaction of 2 moles of isobutane, since H^+ is not a chain carrier. On the other hand, assuming disproportionation of the decyl ion formed from isopentane, one obtains, for example, the stoichiometric equation

$$RF + 3C_5H_{12} \longrightarrow RH + C_6H_{14} + C_4H_{10} + C_5H_{11}^+ + F^-$$

Here the pentyl ion is a chain carrier, hence the number of moles of isopentane converted per mole of alkyl fluoride may be indefinitely large.

NORWOOD, PENNA. RECEIVED SEPTEMBER 29, 1950