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

Reactions of Hydrocarbons Induced by Alkyl Fluoride–Boron Trifluoride. III. Disproportionation of Isohexanes and Isoheptanes in Isobutane Solution[1]

BY ABRAHAM SCHNEIDER AND ROBERT M. KENNEDY

The purpose of this work was to study the ionic disproportionation reactions of isoparaffins of six or more carbon atoms taking place in a medium similar to that existing in the alkylation reaction, namely, in excess isobutane. A well-defined reaction between isobutane and isoparaffins containing six or more carbon atoms was discovered. Treatment of a solution of the isoparaffin in excess isobutane with the combinations alkyl fluoride–boron fluoride or hydrogen fluoride–isobutylene gives rise to a molecule of isopentane and a mixture of isomers containing one carbon atom less than the isoparaffin. Thus, 2,4-dimethylpentane in excess isobutane yields a molecule of isopentane and one of 2,3-dimethylbutane; 2- and 3-methylpentane in solvents of isobutane give less than the predicted two molecules of isopentane, but more than enough to rule out intermolecular disproportion of the hexanes alone as the source of the isopentane. Singly branched isoparaffins enter into this reaction more readily than doubly branched molecules. The heptanes produced in the reaction of 2- and 3-methylpentane with isobutane were largely 2,4- and 2,3-dimethylpentane. This is in marked contrast to the heptane fraction formed in the disproportionation of the hexanes in the absence of isobutane. A mechanism for these reactions is presented and that of the commercial alkylation of alkanes, especially with regard to the formation of "abnormal" products, is discussed.

Introduction

Addition of boron trifluoride to solutions of alkyl fluoride in isoparaffins has been shown to cause the latter to isomerize,[2] disproportionate, and self-alkylate.[3] These solutions which have limited solubility in the hydrocarbon phase initiate fast reactions of isoparaffins at low temperatures and cause the conversion of more than one mole of hydrocarbon per mole of alkyl fluoride. Either component of the system alkyl fluoride–boron trifluoride alone has no action on isoparaffins.

In the alkylation of the butylenes with isobutane using acid catalysts there is always formed a considerable amount of "abnormal" products along with the expected octanes. The major known abnormal products are isopentane, 2,3-dimethylbutane, 2- and 3-methylpentane, 2,3- and 2,4-dimethylpentane, 2- and 3-methylhexane, 2,2,5- and 2,3,5-trimethylhexane.

From a study of the action of boron fluoride on solutions of alkyl fluorides in various isoparaffins, it was observed that a great difference in chemical reactivity exists between isobutane and the higher isoparaffins. The latter demonstrate a certain regularity in their reactions while isobutane is the exception. For example, isobutane treated with an alkyl fluoride and boron fluoride gives predominantly isoöctane and a minor amount of "abnormal" product.[3] On the other hand, isopentane under similar conditions largely disproportionates into isobutane and the methylpentanes. More striking is the result that one mole of alkyl fluoride causes approximately 2 moles of isobutane to react while it effects the conversion of 4.5 moles of isopentane.[3]

The mechanism formulated for the disproportionation reactions of pure isoparaffins containing five or more carbon atoms[3] led us to suspect that in the commercial alkylation of alkanes, where a large excess of isobutane dissolves the product, a reaction between the solvent and the higher isoparaffins might be taking place—this accompanying the better understood reactions between isobutane and the butylenes which form isoöctane.[4]

Experimental

Materials.—The sources, preparation and analysis of the reagents used in this work are described in Papers I and II of this series.[2,3]

Technique.—Apparatus and manipulative details are described in Paper II of this series.[3]

The Reaction between Isobutane and 2-Methylpentane Catalyzed by *t*-Butyl Fluoride and Boron Trifluoride (Expt. No. I).—A 600-cc. copper bomb containing 96 g. of isobutane (1.66 moles), 40 g. of 3-methylpentane (0.47 mole) and 4.5 g. of boron trifluoride (0.066 mole) was maintained at 25° by immersion in a water-bath. Over a period of seven minutes a solution of 22.4 g. of *t*-butyl fluoride (0.30 mole) in 41.2 g. of isobutane (0.71 mole) was introduced causing a pressure rise from 90 to 100 lb./sq. in.

The bomb and its contents were cooled to −78° and the product forced by air pressure into a still-pot containing 100 g. of ice at −78°. The mixture was distilled in a low-temperature column and the residue was separated from the aqueous phase.

Cut 1	−11° to −7°		106.5 g. isobutane
2	− 3 to 15	7.5 cc.	5.5 g.
3	15 to 25	5.8 cc.	3.5 g. largely isopentane
4	25 to 31	21 cc.	15.5 g. isopentane
Residue		78 cc.	54 g.

The residue was separated into two fractions, distillate and residue, by fractionation through a column rated at about 20 plates. Material boiling from 41 to 108° (49 cc.) was distilled in a concentric tube column rated at about 100 theoretical plates and the 0.5-cc. cuts analyzed by infrared (Table I, Expt. No. I). Distillation of the residue from the first fractionation (26 cc., 18.6 g.) through a small column gave 4 cc. boiling from 113.4 to 121° and 5.4 cc. from 121 to 140°.

Addition of Isobutylene to a Solution of 2-Methylpentane in Isobutane Stirred with Anhydrous Hydrofluoric Acid (Expt. No. 8).—A Universal Oil Products type, one liter contactor was charged with 212 g. (10.6 moles) of anhydrous hydrofluoric acid, 102 g. of isobutane (1.76 moles) and 40.5 g. of 2-methylpentane (0.471 mole). With the temperature at 20°, a solution of 20 g. of isobutylene (0.36 mole) in 21 g. of isobutane (0.36 mole) was admitted to the vigorously stirred mixture over a period of three minutes. Stirring was continued for one hour at 30°.

The contents of the autoclave were forced into a copper bomb cooled to −78° and the acid phase separated at this temperature. There resulted 212 g. of acid and 178 g. of organic layer.

The product was placed in a still pot containing 100 g. of a 30% solution of potassium hydroxide in water frozen at −78°. The volatile material was distilled in the low-temperature column:

Cut 1, −8 to −6°, 128 cc., 86 g. isobutane.

The residue (78 g.) was separated from the aqueous phase, dried over potassium carbonate, and distilled further in the low-temperature column

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

[2] A. Schneider and R. M. Kennedy, THIS JOURNAL, **73**, 5013 (1951).

[3] A. Schneider and R. M. Kennedy, *ibid.*, **73**, 5017 (1951).

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

TABLE 1: DISPROPORTIONATION OF ISOHEXANES AND ISOHEPTANE IN EXCESS ISOBUTANE PROMOTED BY *t*-BUTYL FLUORIDE-BORON TRIFLUORIDE

Experiment No.		1	2	3	4	5[a]	6	7	8
Isoparaffin charged		3-Me-pentane	2-Me-pentane	2-Me-pentane	2-Me-pentane	2-Me-pentane	2,3-Di-Me-butane	2,4-Di-Me-pentane	2-Me-pentane
Temperature of bath, °C.		25	26	26	26	27	26	30	20
Charge, g.: (moles)	Isobutane	137.2(2.37)	137 (2.36)	122.8(2.12)	89.6(1.55)	106 (1.83)	139.5(2.41)	140 (2.42)	123 (2.12)
	Higher isoparaffin	40 (0.47)	39 (0.45)	40.0(0.47)	80 (0.93)	40 (0.47)	40 (0.047)	39 (0.39)	40.5(0.47)
	t-Butyl fluoride	22.4(.30)	20 (.26)	46.3(.54)	21.4(.28)	25 (.33)	22.5(.30)	21 (.28)	20 (.36)[h]
	Boron trifluoride	4.5(.066)	5.5(.081)	5.0(.074)	5.0(.074)	5.0(.074)	5.5(.081)	5.0(.074)	212 (10.6)[b]
Product recovered, wt. % of charge		91[c]	93[c]	89[c]	92	91	87[c]	89[c]	93.3
Products, g.,[e] (moles)[f]	Lower layer	[d]	[d]	[d]	6	10	[d]	[d]	212
	Isobutane	106.5(1.84)	111 (1.91)	84.5(1.46)	62 (1.07)	73 (1.26)	118 (2.03)	110.3(1.91)	86 (1.48)
	t-Butyl fluoride	5.5(0.072)	7.5(0.099)	6.5(0.085)	6.5(0.085)	6.0(0.079)	2.1(0.028)	3.2(0.042)	3.4(0.045)
	Isopentane	19 (.26)	18 (.25)	26 (.36)	26 (.36)	19 (.26)	7 (.10)	5.5(.076)	14 (.19)
	C_6	20.2(.235)	20.9(.243)	17.1(.199)	46.0(.53)	21 (.24)	31 (.36)	6.7(.078)	16.5(.192)
	C_7	5.0(.05)	8.2(.082)	7.8(.078)	7.6(.076)	5.4(.054)	4.0(.04)	30.1(.301)	4.6(.046)
	C_8	6.5(.057)	9.8(.086)	15.7(.138)	4.9(.043)	9.1(.080)	12.7(.111)	12.6(.110)	18.1(.159)
	C_9 and higher	22.3	12.0	27.4	21.7	16.3	5.6	13.9	14.4
B. r., °C., of material for fract. and infrared anal.		41-108	30-119		43-98	40-124.5	30-109	36-108	39-135
Vol. % of depentanized product		62.9	65.7		69	75.4	94	74.2	78
Composition of fractionated product, vol. %[g]	C_6 2,3-Dimethylbutane	13.1	11.4		16.0	13.3	53.7	7.1	5.8
	2-Methylpentane	43.4	40.3		42.4	29.2	11.2	2.4	25.0
	3-Methylpentane	16.6	22.7		24.1	11.1	2.0	0.7	10.3
	C_7 2,4-Dimethylpentane	3.4	2.6		0.25	5.9	4.1	46.4	2.3
	2,3-Dimethylpentane	2.3	5.9			3.6	1.9	20.2	6.6
	2-Methylhexane	1.1	0.21		2.7	1.7		0.24	0.81
	3-Methylhexane	0.33	0.07		1.1			0.24	0.68
	n-Heptane		1.2						
	2,2-Dimethylpentane		0.34						
	C_8 2,2,4-Trimethylpentane	2.6	10.1			10.4	16.8	13.8	27.6
	2,3,3-Trimethylpentane								4.0
	2,3,4-Trimethylpentane					1.1			2.9
	2,5-Dimethylhexane					5.2			2.1
	2,4-Dimethylhexane					3.9			1.2
	3,4-Dimethylhexane					1.8			
	C_9 2,2,5-Trimethylhexane								1.1
Unidentified compounds below (°C.), vol. %		(94.9) 3.2	(104)2.81		(76.2)0.0	(119.2)3.4	(99.2)1.5	(93.6)0.14	(117.3) 0
Unidentified compounds above (°C.), vol. %		(94.9)14.2	(104)2.29		(76.2)9.5	(119.2)8.8	(99.2)7.1	(93.6)6.1	(117.3)11.1
Wt. % isobutane converted		22.4	19.1	31.1	30.9	31.1	15.8	21.1	30.2
Wt. % higher isoparaffin converted		48.9	46.6	57.5	42.0	49.0	23.4	23.1	59.5
Moles consumed, higher isoparaffin/isobutane		0.44	0.47	0.41	0.81	0.40	0.29	0.18	0.44

[a] Boron trifluoride was added to solution of the other components. [b] Anhydrous hydrofluoric acid. [c] Does not include wt. of undetermined lower layer. [d] Undetermined. [e] Calculated in part from distillation data. [f] All hexane isomers are considered as recovered starting material. [g] Infrared analysis. [h] Isobutylene.

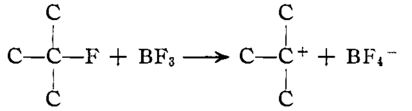
Cut 2	−7 to 12°	3.0 cc.	3.4 g.
	12 to 22	2.2	
3	22 to 30	19	14 g. isopentane
4	30 to 40	3.2 cc.	2 g.

Cut 4 was combined with the residue (53 g.) and the distillation continued in the high-temperature column to separate the charge into two fractions, distillate and residue. The distillate boiling from 39 to 135° (64 cc.) was distilled in a concentric-tube column and the 0.5-cc. cuts analyzed by infrared (Table I, Expt. 8). A rough distillation was performed on the high boiling residue of the initial high-temperature distillation (17.8 cc., 13.0 g.)

Quantity, cc.	B.p., °C.
Initial	138
1	142
2	144
3	145
4	147
5	148
10	157
12	163
14	175
16	200
Residue, 1.8	

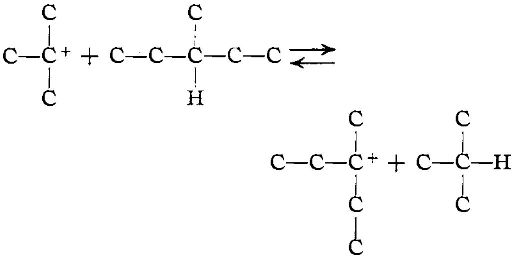
Discussion of Experimental Results

The Reaction between Isobutane and 3-Methylpentane Catalyzed by *t*-Butyl Fluoride and Boron Trifluoride (Expt. No. 1).—In developing a mechanism for the formation of isopentane, the most probable first step is the ionization of *t*-butyl fluoride by the boron fluoride



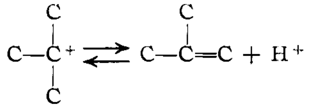
$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}F + BF_3 \longrightarrow C{-}\underset{C}{\overset{C}{C}}{}^{+} + BF_4^-}\qquad (I)$$

As demonstrated by Bartlett, *et al.*,[4] the *t*-butyl ion is reduced to isobutane by abstracting a hydride ion from a tertiary carbon atom of the solvent in a very rapid reaction. There is formed, in this case, the 3-methylpentyl ion, while interaction of the *t*-butyl ion with isobutane produces no net change.

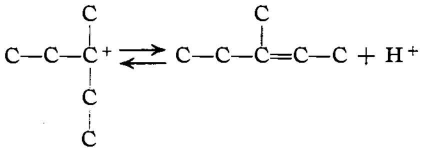


$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{}^{+} + C{-}C{-}\underset{H}{\overset{C}{C}}{-}C{-}C \rightleftarrows C{-}C{-}\underset{\underset{C}{C}}{\overset{C}{C}}{}^{+} + C{-}\underset{C}{\overset{C}{C}}{-}H}\qquad (II)$$

The *t*-butyl and *t*-hexyl ions lose protons to form the corresponding olefins



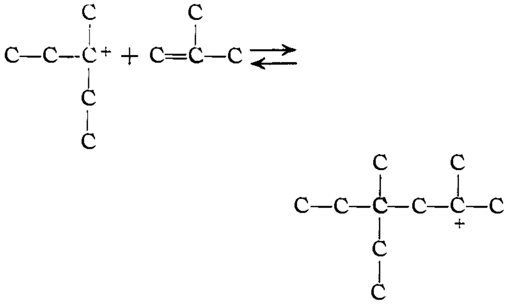
$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{}^{+} \rightleftarrows C{-}\overset{C}{C}{=}C + H^{+}}\qquad (IIIa)$$



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

That the loss of a proton occurs as pictured in IIIb is supported by evidence of Whitmore, *et al.*,[5] who demonstrated that acidic dehydration of *t*-amyl alcohol gives an equilibrium mixture of olefins in which the ratio of trimethylethylene to 2-methylbutene-1 is 7 to 1.

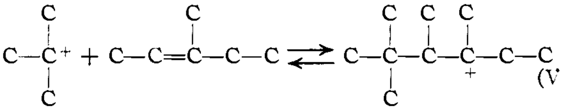
The two carbonium ions and olefins derived from them in IIIa and IIIb may interact in four different ways. A *t*-butyl ion adding to isobutylene ultimately forms trimethylpentane. This is a relatively unfavored sequence of reactions since the amount of 2,2,4- and the other trimethylpentanes formed in this as well as in all the other experiments in which isobutylene was not used is small. The combination of ion with olefin in IIIb has been demonstrated to result in disproportionation into isopentane and isoheptanes ; however, evidence discussed below indicates that this is not the primary source of isopentane observed in the reactions at hand. Combination of the tertiary-hexyl ion with isobutylene gives rise to diisobutylene type carbonium ion for which there exists no simple mechanism of cleavage into C_5 fragments.[3]



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

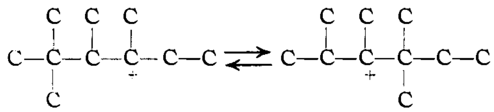
The high boiling residues in these reactions probably contain decanes derived from saturation of this type of reaction intermediates.

Addition of the *t*-butyl ion to the olefin formed in IIIb gives rise to a system studied by Whitmore and Mosher.[6]



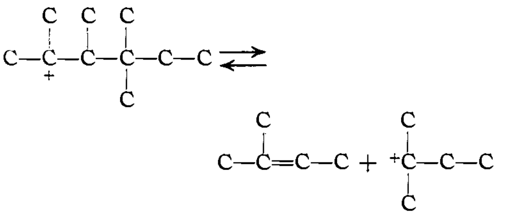
$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{}^{+} + C{-}C{=}\overset{C}{C}{-}C{-}C \rightleftarrows C{-}\underset{C}{\overset{C}{C}}{-}\overset{C}{C}{-}\underset{+}{\overset{C}{C}}{-}C{-}C}\qquad (V)$$

These authors demonstrated that the equilibrium in V lies appreciably to the left at temperatures from 0 to 100°. Further, they proved the existence of a mobile equilibrium between the ion on the right in V and an ion derived from it by a "1,3-shift" of a methyl group



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

The rearranged ion cleaves readily



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

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[5] F. C. Whitmore, *et al.*, THIS JOURNAL, **64**, 2970 (1942).

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

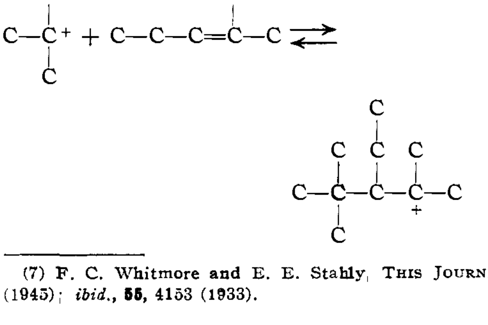
In our system the *t*-amyl ion is converted to isopentane by the one-step reaction of abstracting a tertiary hydride ion from the solvent. On the other hand, trimethylethylene, to be reduced to isopentane, must add a proton and the resulting carbonium ion then undergoes hydrogen exchange. That this occurs is shown by the fact that slightly more than one mole of isopentane is usually found per mole of hexane consumed. Polymerization, alkylation and disproportionation are other paths by which the trimethylethylene may react. This is further discussed below.

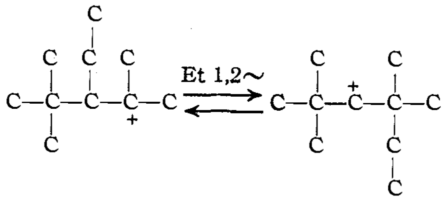
The rearrangement VI and VII to form C_5 fragments correlates the work at hand with the studies of Whitmore[6] on the disproportionation reactions of olefins caused by acid catalysts. Whereas these authors employed amylenes to obtain hexenes and isobutylene, we have studied the reverse of the reaction, starting with a C_4 and C_6 system to yield initially two C_5 fragments. It is apparent that the function of the *t*-butyl fluoride–boron fluoride combination is the introduction of unsaturation into the isoparaffinic solvent.

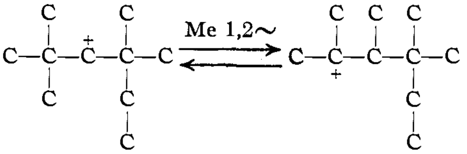
The principle concerned in the cleavage has been stated and exemplified by Whitmore and Stahly,[7] to wit, that an ion of the structure R_3–C–C–C^+ cleaves into smaller fragments when the middle carbon atom has one substituent on it and very readily when it has two.

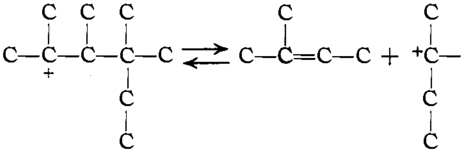
From the mechanism presented it is seen that a mole of isobutane and one of isohexane produce between one and two moles of isopentane. The possibility that all the isopentane might arise from interaction of two hexane molecules is ruled out by the fact that one or more molecules of isopentane are produced for every two molecules of 3-methylpentane consumed. A study of the mechanism of disproportionation of the isohexanes[3] induced under conditions comparable to those employed in the work at hand led to the conclusion that in the absence of side reactions two molecules of hexane react to yield one of isopentane and one of isoheptane. In this experiment, 0.23 mole of 3-methylpentane reacting (in a solvent of isobutane) produced 0.26 mole of isopentane.

The Reaction between Isobutane and 2-Methylpentane Catalyzed by *t*-Butyl Fluoride and Boron Trifluoride (Expt. No. 2).—In formulating a mechanism for the disproportionation, we are obliged to use two normal Wagner-Meerwein shifts rather than the 1,3-methyl shift advocated by Whitmore and Mosher.[6]

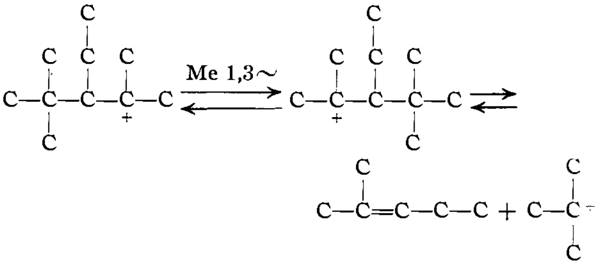

(VIII)


(IX)


(X)


(XI)

On the other hand, a 1,3-methyl shift would give back starting material



This result is not conclusive proof of two, single alkyl group shifts as opposed to the 1,3 shift since 3-methylpentane formed by the rapid isomerization of 2- to 3-methylpentane under these conditions[2] might be the hexane actually reacting (see V, VI and VII).

The small heptane fraction of the product boiling above isopentane consists largely of 2,4- and 2,3-dimethylpentane (Table I, Expt. No. 2). This is in striking difference to the predominant methylhexane content of the heptane fraction derived from disproportionation of pure 2-methylpentane in experiments conducted under conditions comparable with those at hand.[3] The degree of branching of the products of disproportionation of pure isohexanes was found to be essentially the same as that of the starting material. Undoubtedly, the presence of the isobutane solvent is a factor in increasing the degree of branching in the product obtained from this experiment. This is discussed below in the theory of alkylation.

Varying the Conditions in Expt. No. 2.—As would be expected, increasing the amount of *t*-butyl fluoride while maintaining the concentrations of the other components of the reaction constant caused an increase in the yield of isopentane (Expt. No. 3).

Changing the mole ratio of 2-methylpentane to isobutane from 0.19 (Expt. 2) to 0.60 (Expt. 4) while holding the amount of *t*-butyl fluoride constant, increased the yield of isopentane from 0.25 to 0.36 mole. Although the heptane content of the product was small in both experiments, the degree of branching in the experiment with a high ratio

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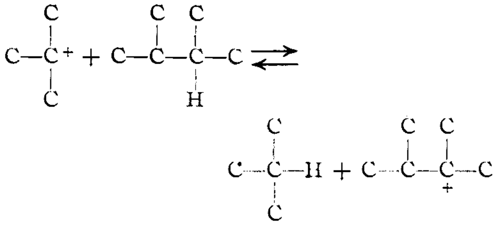
[7] F. C. Whitmore and E. E. Stahly, THIS JOURNAL, **67**, 2158 (1945); *ibid.*, **55**, 4153 (1933).

of hexane to isobutane resembled that of the heptane fraction produced by causing pure 2-methylpentane to disproportionate, in that methylhexanes were predominant (Table I, Expt. No. 4). Determination of the degree of branching is a useful method for distinguishing between disproportionation of two molecules of 2-methylpentane and a reaction involving isobutane.

To ascertain whether an initially high concentration of *t*-butyl fluoride would alter the course of an inter-disproportionation reaction, the method of quickly adding boron fluoride to the other components was used (Table I, Expt. No. 5). There was no appreciable difference in the nature of the product by both methods.

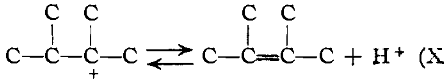
Inter-Disproportionation of Isobutane and 2,3-Dimethylbutane Catalyzed by *t*-Butyl Fluoride and Boron Fluoride (**Expt. No. 6**).—This reaction is of interest since it was found that 2,3-dimethylbutane is rather inert toward entering into reaction with isobutane.

A *t*-butyl ion reacting with 2,3-dimethylbutane forms the tertiary 2,3-dimethylbutyl ion



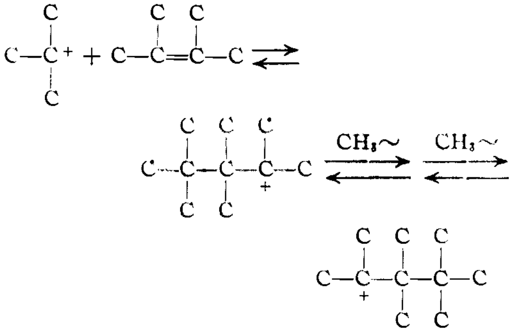
$$\mathrm{C{-}\overset{C}{\underset{C}{C}}{}^{+} + C{-}\overset{C}{C}{-}\overset{C}{\underset{H}{C}}{-}C \rightleftarrows C{-}\overset{C}{\underset{C}{C}}{-}H + C{-}\overset{C}{C}{-}\overset{C}{\underset{+}{C}}{-}C}\qquad \text{(XII)}$$

The hexyl ion readily loses a proton predominantly from the adjacent tertiary carbon.[5]



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

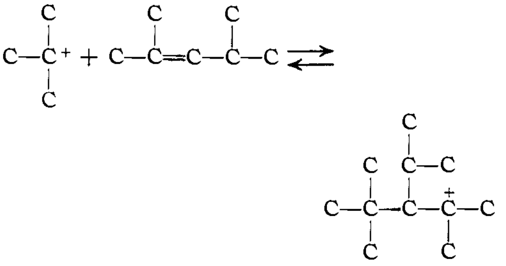
Addition of a *t*-butyl ion to tetramethylethylene gives rise to a very unstable ion.[7] Furthermore, rearrangement of the intermediate ion produces no net change, so that there should be little tendency for reaction to proceed *via* this path



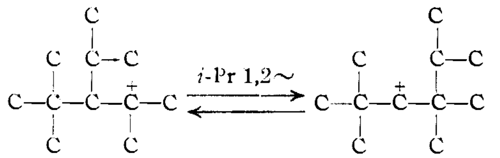
$$\mathrm{C{-}\overset{C}{\underset{C}{C}}{}^{+} + C{-}\overset{C}{C}{=}\overset{C}{C}{-}C \rightleftarrows C{-}\overset{C}{\underset{C}{C}}{-}\overset{C}{\underset{C}{C}}{-}\overset{C}{\underset{+}{C}}{-}C \underset{\longleftarrow}{\xrightarrow{CH_3\sim}} \underset{\longleftarrow}{\xrightarrow{CH_3\sim}} C{-}\overset{C}{\underset{+}{C}}{-}\overset{C}{\underset{C}{C}}{-}\overset{C}{\underset{C}{C}}{-}C}\qquad \text{(XIV)}$$

Inter-Disproportionation of Isobutane and 2,4-Dimethylpentane Catalyzed by *t*-Butyl Fluoride and Boron Trifluoride (**Expt. No. 7**).—The hexane fraction consisted of 2,3-dimethylbutane to the extent of 70%. This is the first example in which a hexane produced in a mixed disproportionation is largely 2,3-dimethylbutane.

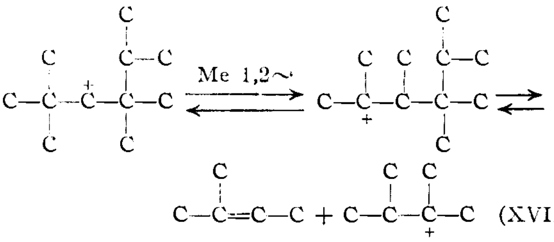
Using the usual sequence of steps we may explain the formation of 2,3-dimethylbutane



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



$$\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}\overset{\overset{C}{C}{-}C}{C}{-}\overset{+}{\underset{C}{C}}{-}C \underset{\longleftarrow}{\xrightarrow{\mathit{i}\text{-}Pr\ 1,2\sim}} C{-}\overset{C}{\underset{C}{C}}{-}\overset{+}{C}{-}\overset{\overset{C}{C}{-}C}{\underset{C}{C}}{-}C}\qquad \text{(XVI)}$$



$$\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}\overset{+}{C}{-}\overset{\overset{C}{C}{-}C}{\underset{C}{C}}{-}C \underset{\longleftarrow}{\xrightarrow{Me\ 1,2\sim}} C{-}\overset{C}{\underset{+}{C}}{-}\overset{C}{C}{-}\overset{\overset{C}{C}{-}C}{\underset{C}{C}}{-}C \rightleftarrows C{-}\overset{C}{C}{=}C{-}C + C{-}\overset{C}{C}{-}\overset{C}{\underset{+}{C}}{-}C}\qquad \text{(XVII)}$$

The 2,3-dimethylbutyl ion is saturated to form a molecule of 2,3-dimethylbutane, and the reduction of trimethylethylene to isopentane appears to be favored. Thus, the over-all reaction is the removal of the central carbon atom of 2,4-dimethylpentane yielding 2,3-dimethylbutane and the building up of isobutane with this carbon atom to give a molecule of isopentane.

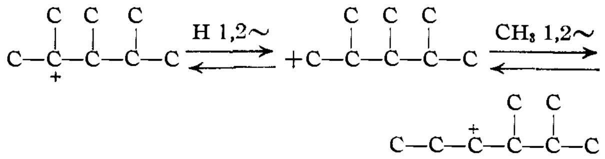
Inter-Disproportionation of Isobutane and 2-Methylpentane Catalyzed by Isobutylene and Hydrogen Fluoride (**Expt. No. 8**).—To correlate the alkyl fluoride–boron fluoride work with hydrogen fluoride alkylation, an experiment using anhydrous hydrogen fluoride and isobutylene was run. The product of this experiment more nearly resembled a typical alkylation in that there was formed a considerable octane fraction (37.8 volume per cent.) composed predominantly of trimethylpentanes. In the cases where alkyl fluorides were the initiators, this was not observed. Apparently, a considerable concentration of isobutylene is necessary to form trimethylpentanes, a condition which seems not to exist in the reactions where *t*-butyl fluoride was caused to ionize in solutions of isobutane and higher isoparaffins.

Theory of the Origin of "Abnormal" Products in the Alkylation Reaction.—The mechanism developed to explain the products of interdisproportionation between isobutane and isohexane or higher isoparaffins may be applied directly to the alkylation reaction. It is postulated that the dimethylpentanes and 2,3-dimethylbutane are formed by reaction of isobutane with dimethylhexanes and dimethylpentanes, respectively. Isopentane is the other product of both disproportionations.

Hydrogen fluoride catalyzed alkylation of pure isobutylene with isobutane[8] gave a product in which the octane fraction was composed of 66.7 volume per cent. of trimethylpentanes and 8.6

[8] Unpublished results of this Laboratory.

of dimethylhexanes. A possible explanation of the formation of dimethylhexanes in this case is the rearrangement of the 2,3,4-trimethylpentyl ion which is an intermediate in the formation of 2,3,4-trimethylpentane.



$$\mathrm{C{-}\underset{+}{\overset{C}{C}}{-}\overset{C}{C}{-}\overset{C}{C}{-}C} \xrightleftharpoons{\mathrm{H\ 1,2\sim}} \mathrm{{+}C{-}\overset{C}{C}{-}\overset{C}{C}{-}\overset{C}{C}{-}C} \xrightleftharpoons{\mathrm{CH_3\ 1,2\sim}} \mathrm{C{-}C{-}\overset{+}{C}{-}\overset{C}{C}{-}\overset{C}{C}{-}C}$$

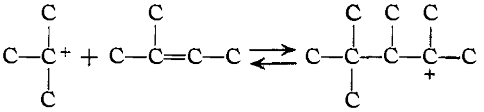
The ion on the right rearranges and is hydrogenated to a mixture of all the dimethylhexanes. This rearrangement resembles that which occurs when 2,3-dimethylbutane is subjected to the alkyl fluoride–boron fluoride system.[2] In the alkylation of the normal butylenes with isobutane, dimethylhexanes are a primary product.[9] The dimethylhexanes undergo reaction with isobutane to form dimethylpentanes and isopentane in a series of reactions similar to that outlined above for the inter-disproportionation of 2,4-dimethylpentane with isobutane.

The reaction of 2,3-dimethylhexane with isobutane is of the same type as that of 2,3-dimethylbutane with isobutane and consequently would be expected to be unfavored. The formation of 2,3-dimethylbutane and isopentane from dimethylpentanes and isobutane has been demonstrated experimentally (Table I, Expt. No. 7).

It is of interest to present data of Webb and Galloway[10] on the infrared analysis of hydrogen fluoride catalyzed isobutane–butylene alkylates. In 16 alkylates the volume per cent. of dimethylhexanes exceeds that of the dimethylpentanes and these, in turn, are larger in amount than 2,3-dimethylbutane. This is in confirmation of the theory that the dimethylhexanes are the precursors of the various abnormal products of alkylation. Methylhexanes and methylheptanes are present only in very small amounts.

2,2,4-Trimethylpentane is inert toward entering into the disproportionation reaction with isobutane under the conditions existing in the normal alkylation reaction. The success of the alkylation reaction in producing large amounts of trimethylpentanes can be attributed to this fact. The non-reactive tertiary hydrogen of isoöctane in this type of system has no explanation.

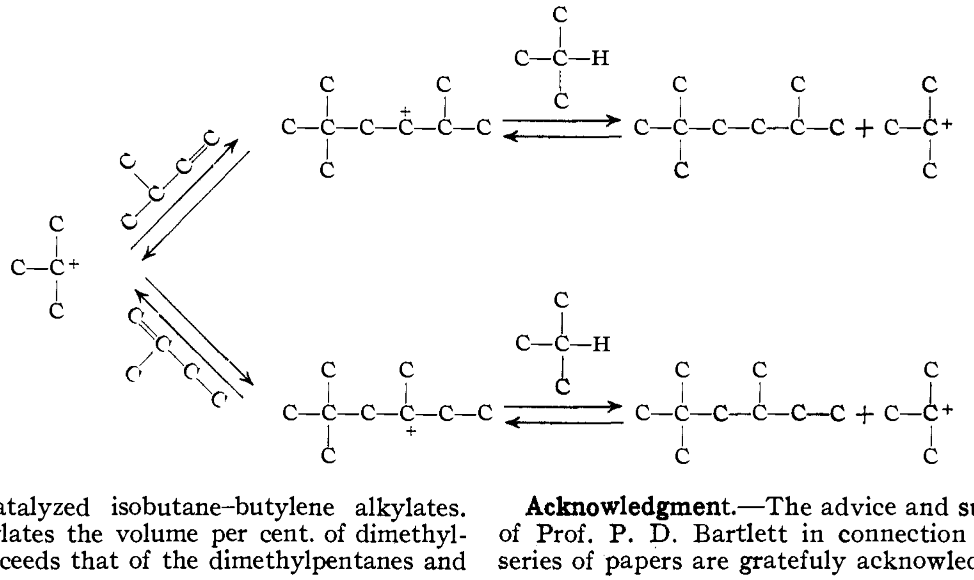
Each of the inter-disproportionation reactions produces trimethylethylene as one of the reaction products. The olefin may be saturated to form isopentane or react with a *t*-butyl ion.



$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{}^{+}} + \mathrm{C{-}\overset{C}{C}{=}C{-}C} \rightleftharpoons \mathrm{C{-}\underset{C}{\overset{C}{C}}{-}\overset{C}{C}{-}\underset{+}{\overset{C}{C}}{-}C}$$

(XVIII)

This ion is unstable and the equilibrium is far to the left.[7] Whereas trimethylethylene is formed in largest amounts in reactions involving loss of a proton from the *t*-amyl ion, the equilibrium mixture contains a small amount of isopropylethylene and a somewhat larger amount of 2-methylbutene-1.[5] The *t*-butyl ion adding to these olefins forms stable intermediates which on abstraction of hydride ions from the solvent are converted to 2,2,5- and 2,2,4-trimethylhexane[11]



Acknowledgment.—The advice and suggestions of Prof. P. D. Bartlett in connection with this series of papers are grateful acknowledged.

NORWOOD, PA.

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[9] M. H. Gorin, C. S. Kuhn and C. B. Miles, *Ind. Eng. Chem.*, **38**, 795 (1946).

[10] G. M. Webb and W. S. Galloway, *Pet. Processing*, **2**, 444 (1947).

[11] Patent applications have been filed by the Sun Oil Company on material in this series considered to be patentable.