Treatment of the lactone with methyl-alcoholic ammonia at room temperature furnished the crystalline amide of 2,3,5-trimethyl-*l*-arabonic acid in good yield and established the furanose structure of the original pentoside; m. p. 136° (from acetone); specific rotation +20° (18°, *c* 2, water).

Anal. Calcd. for $C_8H_{17}O_5N$: OCH_3, 44.9; N, 6.7. Found: OCH_3, 44.9; N, 6.8.

Identification of 2,4-Dimethyl-*d*-galactose.—Fraction VII, Table II, crystallized spontaneously and was dissolved in methyl alcohol. Partial crystallization took place upon standing and recrystallization from methanol gave β-methyl-2,4-dimethyl-*d*-galactoside; m. p. 165°,[8] specific rotation not measurable (20°, *c* 5, water). The residual sirup freed from methyl alcohol, partially crystallized from acetone solution and after recrystallization from the same solvent furnished α-methyl-2,4-dimethyl-*d*-galactoside; m. p. 105°,[8] specific rotation +145° (20°, *c* 2, water).

Hydrolysis of both isomers, and the residual sirup (2 g.) with 25 cc. of *N* sulfuric acid on a boiling water-bath for ten hours gave 2,4-dimethyl-galactose and this, upon treatment with aniline (1 cc.) in ethanol solution under reflux for three hours, gave the anilide upon removal of solvent. Recrystallization from methanol furnished the anilide of 2,4-dimethyl-*d*-galactose in good yield; m. p. 215°.[9]

Anal. Calcd. for $C_{14}H_{21}O_5N$: OCH_3, 21.9; N, 5.2. Found: OCH_3, 21.9; N, 5.2.

Summary

1. The methyl ether of mesquite gum has been prepared by treatment of the polysaccharide with dimethyl sulfate and alkali.

2. Methanolysis of mesquite gum methyl ether using methanol–hydrogen chloride yields a sirup which is shown to contain 2,3,5-trimethyl-methyl-arabinoside, 3,5-dimethyl-methyl-arabinoside, 2,4-dimethyl-methyl-galactoside and 2,3,4-trimethyl-methyl-glucuronoside.

3. The ratio of the above components was found to be as 1:3:2:1, respectively. The ratio of arabinose to galactose to methoxy-glucuronic acid in mesquite gum is therefore 4:2:1.

4. From these data it is concluded that one molecule of methoxy-glucuronic acid and one of arabinose occupy terminal positions in the repeating unit of mesquite gum. The remaining units of arabinose are joined by glycosidic linkage at the first and second carbon atoms while the galactose residues are trebly linked at the first, third and six positions.

MOSCOW, IDAHO RECEIVED OCTOBER 9, 1945

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[8] Smith, *J. Chem. Soc.*, 1736 (1939).

[9] Smith, *ibid.*, 1737 (1939).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF UNIVERSAL OIL PRODUCTS COMPANY]

The Mechanism of the Alkylation of Paraffins. II. Alkylation of Isobutane with Propene, 1-Butene and 2-Butene

BY LOUIS SCHMERLING

In connection with the study of the mechanism of the alkylation of isoparaffins with olefins, it became of interest to compare the products obtained by the alkylation of isobutane with 1-butene and with 2-butene. According to the recently proposed alkylation mechanism,[1] these butenes should yield different octanes as the major alkylation products. The literature contains no comparative data on the structure of the isobutane alkylates obtained with pure 1-butene and with pure 2-butene in the presence of aluminum chloride. In the present paper experiments which were carried out to obtain the desired information are described and the results are discussed in the light of the proposed mechanism of the reaction.

The use of anhydrous aluminum chloride as catalyst for the alkylation of isobutane with olefins often results in a complex mixture of products because of the ease with which secondary reactions (especially isomerization, cracking and hydrogen transfer) occur. Formation of by-products in the case of alkylation by propene and butenes may be greatly minimized by carrying out the reaction at −35°.[2] An alternative means of preventing their formation consists in so modifying the catalyst as to decrease its activity for the side reactions without substantially affecting its alkylating activity. A modification which was found to be particularly suitable and which was therefore used in the present investigation consists of the addition complex of equimolecular amounts of aluminum chloride and methanol, $AlCl_3 \cdot CH_3OH$.

Aluminum chloride monomethanolate is a crystalline compound which is stable at temperatures below 70°; at higher temperatures it decomposes, forming hydrogen chloride and methoxyaluminum dichloride, further heating of which yields methyl chloride and oxyaluminum chloride.[3] It very readily catalyzes the alkylation of benzene, in which it is soluble, and of isobutane, in which it is not. On the other hand, the product of the reaction of aluminum chloride with two molecular proportions of methanol (*i. e.*, $AlCl_3 \cdot 2CH_3OH$) is not an alkylation catalyst.

Tables I and II summarize the results obtained by the alkylation of isobutane with 1-butene and with 2-butene in the presence of aluminum chloride monomethanolate, hydrogen chloride being used as promoter. Data for the alkylations in the presence of aluminum chloride are included for purpose of comparison.

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[1] L. Schmerling, THIS JOURNAL, **66**, 1422 (1944); **67**, 1778 (1945).

[2] H. Pines, A. V. Grosse and V. N. Ipatieff, *ibid.*, **64**, 33 (1942).

[3] J. F. Norris and B. M. Sturgis, *ibid.*, **61**, 1413 (1939).

It will be observed at once that the use of pure aluminum chloride as catalyst resulted in an alkylate which consisted of a very complex mixture of isoparaffins. Octanes were formed in largest amount, but the yields of isopentane and branched-chain hexanes and heptanes were also

TABLE I

ALKYLATION OF ISOBUTANE WITH OLEFINS

Experiment no.	1	2	3	4	5	6	7
Catalyst	$AlCl_3$		$AlCl_3 \cdot CH_3OH$				
Olefin	1-Butene	2-Butene	1-Butene		2-Butene		Propene
Reaction temperature, °C.	30	30	28	55	28	64	63
Alkylate							
Yield, %[a]	165	140	85	160	148	150	185
Chlorine content, %	0.03	0.18	..	1.0	1.6	1.9	0.58
Gasoline, I. B. p. −125°							
Yield, % by vol. of alkylate	74	75	30	84	86	73	90
Octane No., M. M.	74.5	83.5	..	76.1	94.1	92.4	85.0[b]
Composition of alkylate % by wt. of total alkylate							
Isopentane	17.1	13.1		..[c]	..[c]	..[c]	1.1
Alkyl chloride	..	..		3.1[d]	3.8[e]	11.2	0.5
Dimethylbutanes	6.1	7.5		1.7	3.8		2.8
Methylpentanes	8.1	6.4		1.5	..	3.7	..
Trimethylbutane	0.6	0.7		..	..	..	..
Dimethylpentanes	5.3	5.6		5.7	5.0	..	52.2
Methylhexanes	5.3	3.9		..	..	..	..
Trimethylpentanes	6.4	14.5		9.5	65.1	44.2	7.3
Dimethylhexanes	11.5	6.8		59.9	3.8	7.3	1.5
Methylheptanes	3.5	2.6		..	..	..	..
Nonanes and higher	36.1	38.9		18.6	18.5	33.6	34.6

[a] % by weight of olefin. The quality of the product (especially with $AlCl_3 \cdot CH_3OH$ as catalyst) indicates that the values given are lower than the true yields. The cause of this discrepancy has not been determined. [b] Octane number of 165° end-point gasoline. [c] Values given are on a pentane-free basis. Relatively little pentane was formed. [d] *s*-Butyl chloride. Corresponds to 1.2% chlorine in alkylate. [e] Consists of 3.3% *s*-butyl chloride and 0.5% *t*-butyl chloride. Corresponds to 1.5% chlorine in alkylate.

TABLE II

COMPOSITION OF 125° END-POINT PRODUCTS PREPARED BY THE ALKYLATION OF ISOBUTANE WITH OLEFINS

Experiment no.	1	2	4	5	6	7
Catalyst	$AlCl_3$		$AlCl_3 \cdot CH_3OH$			
Olefin	1-Butene	2-Butene	1-Butene	2-Butene		Propene
Reaction temperature, °C.	30	30	55	28	64	63
Composition of product, % by wt. of gasoline						
Isopentane	23.1	17.4	..[a]	..[a]	..[a]	1.6
Alkyl chloride	..	..	3.7	4.4	15.3	0.6
2,2-Dimethylbutane	4.1	5.4	..	..		..
2,3-	4.8	5.7	2.0	4.4		3.9
2-Methylpentane	7.7	6.6	1.8	..	..	..
3-	4.1	2.7	..	..	..	..
2,2,3-Trimethylbutane	1.0	1.0	..	..	..	..
2,2-Dimethylpentane	0.3	0.2	..	..	..	..
2,4-	5.1	5.5	4.9	3.7	2.1	33.3
2,3-	2.1	2.4	1.9	2.2	3.0	35.2
x-Methylhexanes	7.5	5.7	..	..	..	..
2,2,4-Trimethylpentane	3.9	12.8	8.0	33.1	29.8	4.4
2,2,3-	1.0	1.3	..	0.6	1.7	..
2,3,4-	2.0	2.9	3.3	26.3	18.6	3.1
2,3,3-	1.9	2.6	..	16.3	10.5	1.7
2,4- and 2,5-Dimethylhexane	13.2	8.1	41.2	3.8	8.5	1.4
2,2-	0.5	0.5	..	..	..	..
2,3-	1.9	0.7	21.0	0.7	1.5	0.7
3,4-	..	..	9.2	..	..	..
x-Methylheptanes	4.8	3.6	..	..	..	..
Nonanes and higher	11.0	14.9	3.0	4.5	9.0	14.1

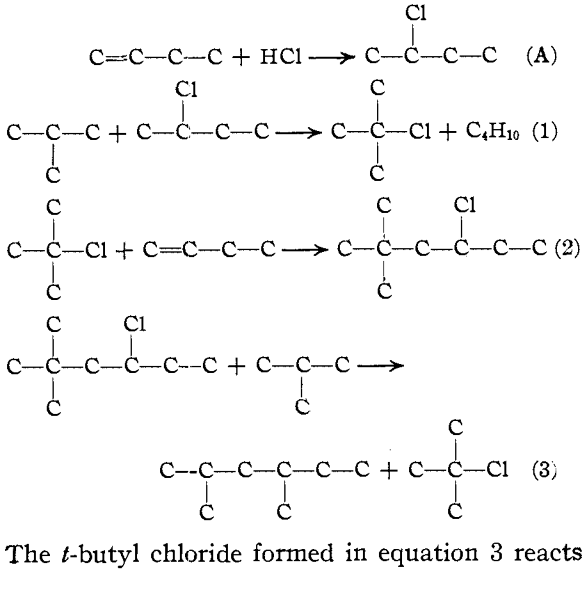
[a] Values given are on a pentane-free basis. Relatively little pentane was formed.

high. The secondary reactions which yielded these lower boiling paraffins as well as those which produced the large amount of higher boiling material were markedly diminished by use of the methanol-modified catalyst.

The most significant point to be noted from Tables I and II and from Figs. 1 and 2 is that, although the products obtained at the temperatures which gave best results for the two butenes were very similar in so far as yield and range of boiling point were concerned, the product of 1-butene alkylation contained about 60% by weight of dimethylhexanes and 10% of trimethylpentanes, whereas the 2-butene product (obtained at 28°) contained 65% of trimethylpentanes and only 4% of dimethylhexanes. The difference in composition of the products is apparent also in the octane numbers of the 125° end-point gasolines. That from the 1-butene had an octane number of only 76.1 and that from 2-butene, 94.1.

Although the alkylation with 1-butene proceeded very smoothly at 55° in the presence of aluminum chloride monomethanolate, relatively little alkylation occurred at room temperature. That the ease of alkylation at the higher temperature was not due to isomerization of 1-butene into 2-butene is evident from the composition of the product. Use of a higher temperature (64°) than room temperature with 2-butene resulted in the formation of an alkylate containing a larger percentage of higher boiling material, as well as of a gasoline which had a slightly lower octane number owing to the presence of somewhat more dimethylhexanes and less trimethylpentanes.

Mechanism of Alkylation with 1-Butene.—The formation of dimethylhexanes as the chief product in one case and not in the other is very readily explained by the recently described alkylation mechanism.[1] Thus, for the alkylation with 1-butene



$$\mathrm{C{=}C{-}C{-}C + HCl \longrightarrow C{-}\overset{\overset{Cl}{|}}{C}{-}C{-}C} \qquad \text{(A)}$$

$$\mathrm{C{-}\underset{\underset{C}{|}}{C}{-}C + C{-}\overset{\overset{Cl}{|}}{C}{-}C{-}C \longrightarrow C{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{-}Cl + C_4H_{10}} \qquad (1)$$

$$\mathrm{C{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{-}Cl + C{=}C{-}C{-}C \longrightarrow C{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{-}C{-}\overset{\overset{Cl}{|}}{C}{-}C{-}C} \qquad (2)$$

$$\mathrm{C{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{-}C{-}\overset{\overset{Cl}{|}}{C}{-}C{-}C + C{-}\underset{\underset{C}{|}}{C}{-}C \longrightarrow}$$

$$\mathrm{C{-}\underset{\underset{C}{|}}{C}{-}C{-}\underset{\underset{C}{|}}{C}{-}C{-}C + C{-}\overset{\overset{C}{|}}{\underset{\underset{C}{|}}{C}}{-}Cl} \qquad (3)$$

The *t*-butyl chloride formed in equation 3 reacts with 1-butene as in equation 2 and the cycle is repeated. The reaction of equation 1 serves as an initiating reaction only.

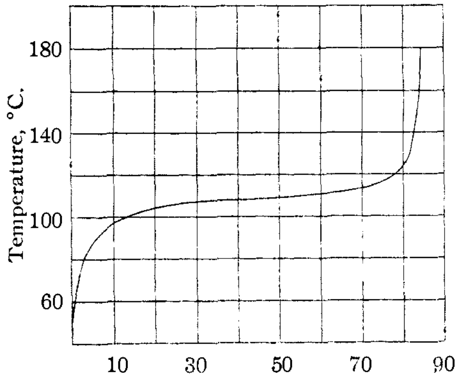


Fig. 1.—Distillation of liquid product of the reaction of isobutane with 1-butene at 55°.

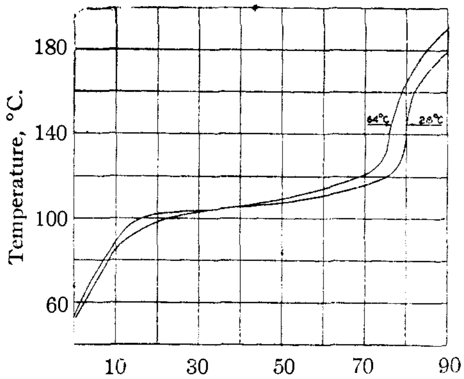


Fig. 2.—Distillation of liquid product of the reaction of isobutane with 2-butene.

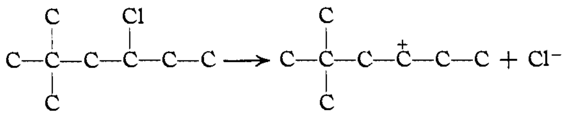
The rearrangement of the chlorooöctane (3-chloro-5,5-dimethylhexane) as in equation 3 is to be expected. It is readily explained by Whitmore's "common basis of intramolecular rearrangements,"[4] now usually referred to as the "carbonium ion" theory,[5] which is illustrated in the equations below.

The tertiary carbonium ions (or tertiary alkyl chlorides) designated as I, II and III are converted to paraffins by reaction with hydrogen donated by isobutane, as indicated by equation 3. It will be noted that formation of II and III is indicated as occurring by way of 1,3 and 1,4 shifts of methyl groups. While a 1,3 shift may be possible, this and the longer distance rearrangement may actually proceed by means of a series of 1,2 shifts.

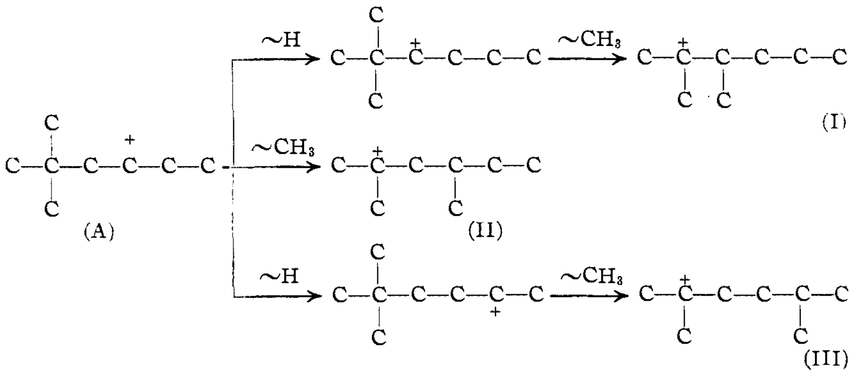
Formation of 3,4-dimethylhexane can be explained only by assuming that several inter-

(4) F. C. Whitmore, THIS JOURNAL, **54**, 3274 (1932).

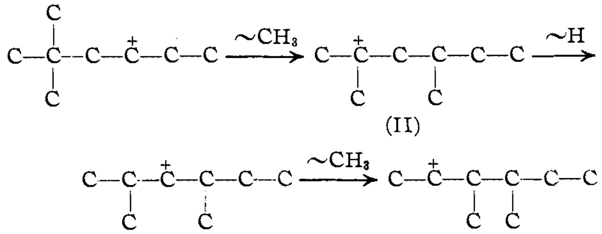
(5) The reactions of equations 1 and 3 may, of course, also be expressed in terms of this theory. See P. D. Bartlett, F. E. Condon and A. Schneider, *ibid.*, **66**, 1534 (1944).



$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}C{-}\overset{Cl}{C}{-}C{-}C \longrightarrow C{-}\underset{C}{\overset{C}{C}}{-}C{-}\overset{+}{C}{-}C{-}C + Cl^-}$$



mediate rearrangements of the original carbonium ion (A) occur

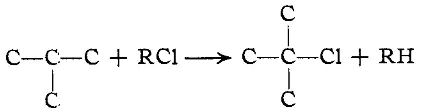


$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}C{-}\overset{+}{C}{-}C{-}C \xrightarrow{\sim CH_3} C{-}\underset{C}{\overset{+}{C}}{-}C{-}\underset{C}{C}{-}C{-}C \xrightarrow{\sim H}}$$

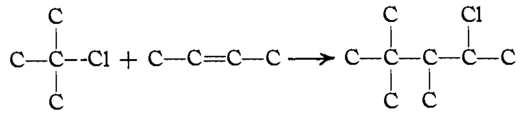
(II)

$$\mathrm{C{-}\underset{C}{C}{-}\overset{+}{C}{-}\underset{C}{C}{-}C{-}C \xrightarrow{\sim CH_3} C{-}\overset{+}{C}{-}\underset{C}{C}{-}\underset{C}{C}{-}C{-}C}$$

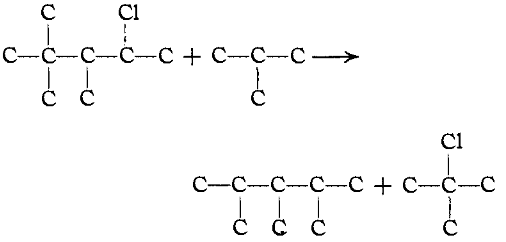
Mechanism of Alkylation with 2-Butene.—The alkylation of isobutane with 2-butene may be outlined in similar manner



$$\mathrm{C{-}\underset{C}{C}{-}C + RCl \longrightarrow C{-}\underset{C}{\overset{C}{C}}{-}Cl + RH} \quad (1')$$



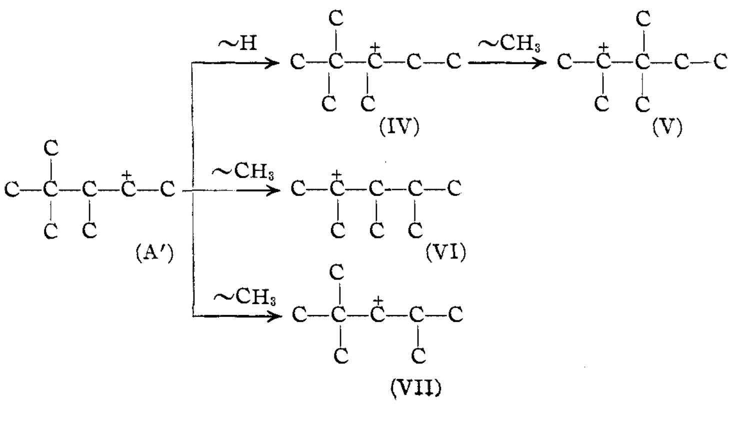
$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}Cl + C{-}C{=}C{-}C \longrightarrow C{-}\underset{C}{\overset{C}{C}}{-}\underset{C}{C}{-}\overset{Cl}{C}{-}C} \quad (2')$$



$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}\underset{C}{C}{-}\overset{Cl}{C}{-}C + C{-}\underset{C}{C}{-}C \longrightarrow C{-}\underset{C}{C}{-}\underset{C}{C}{-}\underset{C}{C}{-}C + C{-}\underset{C}{\overset{Cl}{C}}{-}C} \quad (3')$$

Evidence in support of the reactions of equations 2 and 2′ was obtained by showing[6] that the addition of *t*-butyl chloride to 1- and 2-butene yields chlorooöctanes having the 2,2-dimethylhexane and 2,2,3-trimethylpentane structure, respectively. In the case of the latter, there are indications that the secondary chloride shown in equation 2′ is isomerized to a large extent into 3-chloro-2,2,3-trimethylpentane—*i. e.*, the chloride corresponding to IV.

The rearrangement may be formulated as is shown in IV, V, VI and VII.



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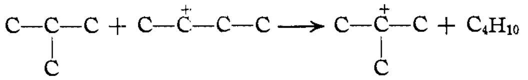
[6] L. Schmerling, to be published.

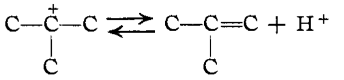
Addition of a negative hydrogen ion (from isobutane) to the carbonium ion (IV) would yield 2,2,3-trimethylpentane. Because very little of this octane is obtained, it must be concluded that IV is very unstable and rearranges to V too readily to permit its conversion into isoparaffin.

The migration of a tertiary methyl group such as is involved in the formation of VII occurs to a relatively small extent and it seems probable that only a small part, if any, of the 2,2,4-trimethylpentane found in the alkylate is derived from this source. On the other hand, formation of this carbonium ion might explain why more 2,2,4-trimethylpentane is obtained with 2-butene than with 1-butene. Production of the 2,2,4-trimethylpentane, in the latter case, as well as much or perhaps all in the former, may be explained by the following reactions (expressed in terms of carbonium ions for purposes of illustration)

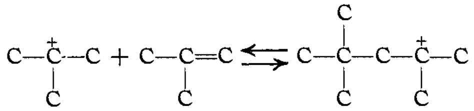
$$C{=}C{-}C{-}C + H^+ + Cl^- \rightleftarrows C{-}\overset{+}{C}{-}C{-}C + Cl^- \quad (4)$$



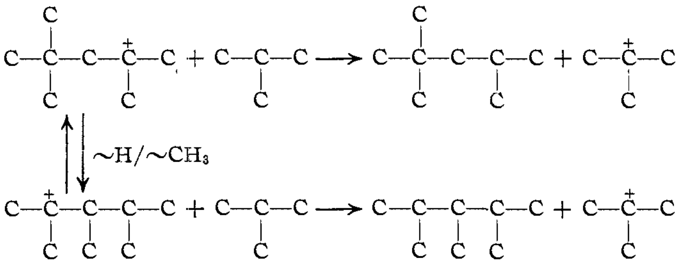
$$\underset{\overset{|}{C}}{C{-}C{-}C} + C{-}\overset{+}{C}{-}C{-}C \longrightarrow C{-}\underset{\overset{|}{C}}{\overset{+}{C}}{-}C + C_4H_{10} \quad (5)$$



$$C{-}\underset{\overset{|}{C}}{\overset{+}{C}}{-}C \rightleftarrows C{-}\underset{\overset{|}{C}}{C}{=}C + H^+ \quad (6)$$



$$C{-}\underset{\overset{|}{C}}{\overset{+}{C}}{-}C + C{-}\underset{\overset{|}{C}}{C}{=}C \rightleftarrows C{-}\underset{\overset{|}{C}}{\overset{\overset{C}{|}}{C}}{-}C{-}\underset{\overset{|}{C}}{\overset{+}{C}}{-}C \quad (7)$$



$$C{-}\underset{\overset{|}{C}}{\overset{\overset{C}{|}}{C}}{-}C{-}\underset{\overset{|}{C}}{\overset{+}{C}}{-}C + C{-}\underset{\overset{|}{C}}{C}{-}C \longrightarrow C{-}\underset{\overset{|}{C}}{\overset{\overset{C}{|}}{C}}{-}C{-}\underset{\overset{|}{C}}{C}{-}C + C{-}\underset{\overset{|}{C}}{\overset{+}{C}}{-}C \quad (8)$$

$$\Big\updownarrow \sim H/\sim CH_3$$

$$C{-}\underset{\overset{|}{C}}{\overset{+}{C}}{-}\underset{\overset{|}{C}}{C}{-}\underset{\overset{|}{C}}{C}{-}C + C{-}\underset{\overset{|}{C}}{C}{-}C \longrightarrow C{-}\underset{\overset{|}{C}}{C}{-}\underset{\overset{|}{C}}{C}{-}\underset{\overset{|}{C}}{C}{-}C + C{-}\underset{\overset{|}{C}}{\overset{+}{C}}{-}C$$

The over-all reaction may be written

$$2\ i\text{-}C_4H_{10} + C_4H_8 \longrightarrow C_8H_{18} + C_4H_{10} \quad (9)$$

Its net effect is one of hydrogen transfer with resultant saturation of the olefinic double bond.

Conversion of Butene to Butane.—It will be noted from equation 9 and its component reactions that one molecule of butane must be formed for each molecule of 2,2,4- or 2,3,4-trimethylpentane obtained in alkylation with 1-butene. Also, conversion of butene to butane must accompany the formation of at least part of the 2,2,4-trimethylpentane obtained with 2-butene.

When aluminum chloride methanolate is used as catalyst for the alkylation of isobutane with 1- or 2-butene, the exit gas contains very little or no *n*-butane despite the fact that an appreciable quantity of 2,2,4-trimethylpentane is produced. This apparent discrepancy in the alkylation mechanism may readily be explained. The *n*-butene is converted not into *n*-butane but into isobutane which, of course, cannot be differentiated from the isobutane charge. In other words, the hydrogen–chlorine exchange reaction of equation 1 (or the proton transfer of equation 5) is accompanied by rearrangement of the carbon skeleton of the *s*-butyl chloride (or the *s*-butyl carbonium ion).

On the other hand, a considerable amount of *n*-butane was present in the gaseous product from the reaction of isobutane with either normal butene in the presence of pure aluminum chloride. In experiment 2, for example, the butane fraction consisted of 84% isobutane and 16% *n*-butane; this *n*-butane corresponded to 35–40% by weight of the 2-butene charge. However, the 2-butene was not necessarily the source of the *n*-butane. Instead, the *n*-butane was probably formed by the isomerization of isobutane in the presence of the more active aluminum chloride catalyst. The equilibrium mixture of *n*- and isobutane at 30° contains 20.0% of the straight chain compound.[7]

Inferential evidence in support of the above given explanation may be seen in the work of Pines and Ipatieff[8] on the reaction of methylcyclopentane with olefins in the presence of sulfuric acid. Thus, the reaction of the cycloparaffin with 2-pentene resulted chiefly in hydrogen transfer to the olefin to form isopentane, and not *n*-pentane. Similarly, the reaction of "*n*-butene" resulted in the conversion of about 10% of the olefin to butane, 30% of which was isobutane.

Comparison of Aluminum Chloride, Hydrogen Fluoride and Sulfuric Acid Alkylates.—It is apparent from the above results and discussion that markedly different products are obtained in the alkylation of isobutane with 1-butene and with 2-butene when aluminum chloride catalysts are used. Even with the pure (unmodified) metal halide as catalyst, the gasoline obtained from the 2-butene alkylation again had a higher octane number (83.5) than did that from the 1-butene reaction (74.5), the difference being due to the presence of about twice as much trimethylpentanes and only half as much dimethylhexanes in the former product.

When, on the other hand, hydrogen fluoride is used as alkylation catalyst, there is only a relatively small difference in the character of the products obtained with the two *n*-butenes.[9] The oc-

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(7) H. Pines, B. Kvetinskas, L. S. Kassel and V. N. Ipatieff, THIS JOURNAL, **67**, 631 (1945).

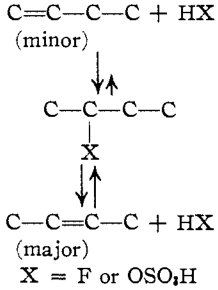
(8) H. Pines and V. N. Ipatieff, paper presented before the Petroleum Division of the American Chemical Society at the Cleveland Meeting, April, 1944.

(9) C. B. Linn and A. V. Grosse, paper presented before the Petroleum Division of the American Chemical Society at the Cleveland Meeting, April, 1944.

tane numbers of the 150° end-point gasolines prepared by the alkylation of isobutane with 1- and 2-butene, respectively, were 92.7 and 95.3.

Although no similar comparative data for the alkylation in the presence of sulfuric acid as catalyst have been published, it has been stated[10] that "the reaction-products obtained from the normal butylenes are quite similar to those obtained from the isobutylene except for the amount of light ends formed." Irreversible isomerization of 1-butene into an equilibrium mixture of 2-butene and methylpropene was assumed to occur prior to reaction with the isobutane.

A possible explanation of the difference in the behavior of the metal halide catalysts and that of the acid catalysts may be based on the presumption that the reaction which occurs most rapidly, when a mixture of isobutane and 1- or 2-butene comes in contact with liquid hydrogen fluoride or sulfuric acid, is the addition of the acid to the olefin to form *s*-butyl ester. There would then exist in the reaction mass an equilibrium mixture which may be described by the following



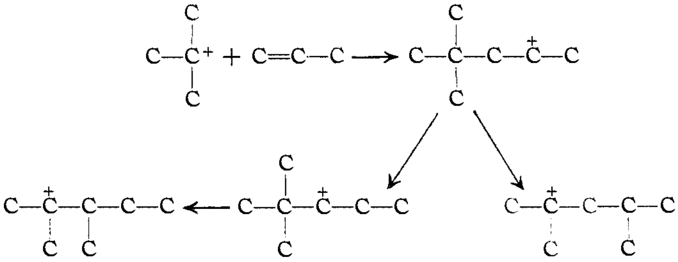
(10)

Octanes produced *via* the addition of *t*-butyl ester (from isobutane) to the butenes so formed would be the same regardless of what alkylating agent is used[11] and the product would contain more trimethylpentanes than dimethylhexanes. If *all* of the alkylate were produced through the olefins formed as in equation 10, all three alkylating agents (1-butene, 2-butene and *s*-butyl ester) would yield *identical* products. However, formation of part of the alkylate in the case of the butenes by the direct reaction of the *t*-butyl ester with the olefin before the olefin has reacted with the acid catalyst would account for the small differences in composition.

With aluminum chloride catalysts, on the other hand, the reaction proceeds chiefly via the addition of *t*-butyl chloride to the original butene before more than a relatively minor portion of the latter can react with the hydrogen chloride promoter to yield *s*-butyl chloride. Therefore, the two *n*-butenes yield very different alkylates.

Methylpropene will yield trimethylpentanes as the primary products. There seems to be little need for the postulation[10] of the intermediate isomerization of 2-butene to methylpropene.

Alkylation of Isobutane with Propene.—Relatively little side reaction occurred when isobutane was alkylated with propene in the presence of aluminum chloride monomethanolate and hydrogen chloride. As may be seen from the results presented in Tables I and II, more than half of the liquid product was heptane and consisted of appoximately equal amounts of 2,3- and 2,4-dimethylpentane. Propane was formed to the extent of only about 4.5% by weight of the propene charged; trimethylpentanes formed by the "self-condensation" of isobutane (*cf.* equation 9) were formed in correspondingly small amount.



The formation of the dimethylpentanes as the major product of the alkylation is to be expected (see above).

Experimental

Materials: Isobutane. Phillips Petroleum Company product of at least 99% purity. **1- and 2-Butene:** Phillips Petroleum Company, Technical grade of over 95% purity. Each olefin contained approximately 2% of the other. **Propene:** Matheson Company, 99% pure. **Aluminum Chloride:** The commercially available metal halide was resublimed by heating at 230°. **Aluminum Chloride Monomethanolate:** Methanol (12.8 g., 0.4 mole) which had been precooled to about −50° was added dropwise to 53.3 g. (0.4 mole) of resublimed aluminum chloride powder in a flask immersed in a Dry Ice–acetone bath. The aluminum chloride was stirred vigorously during the addition which usually required about five minutes. White fumes (apparently a mixture of hydrogen chloride and an oxy compound of aluminum) were evolved in small amount. The reaction product, which was a white lumpy solid, was allowed to warm to room temperature and was then heated to 50–60° by means of a water-bath. A clear or slightly turbid pale yellow liquid was thus obtained. The melt crystallized when cooled to room temperature. The loss in weight of the mixture during mixing and heating usually was about 2 g. **Aluminum chloride dimethanolate** was prepared in similar manner, 12.8 g. (0.4 mole) of cold methanol being added dropwise to 26.7 g. (0.2 mole) of resublimed aluminum chloride in the flask immersed in a Dry Ice–acetone bath. Hydrogen chloride was evolved during the addition. The product, liquid at 60° and solid at room temperature, weighed 36.5 g.

Apparatus and Procedure.—The alkylations were carried out in a one-liter stainless steel autoclave equipped with a very efficient stirrer (a "turbo-mixer"). The reaction temperature was maintained by a water-bath. The catalyst (15 g. of resublimed aluminum chloride or 20 g.

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[10] S. H. McAllister, J. Anderson, S. A. Ballard and W. E. Ross, *J. Org. Chem.*, **6**, 647 (1941). See, also, S. F. Birch and A. E. Dunstan, *Trans. Faraday Soc.*, **35**, 1013 (1939).

[11] C. B. Linn has shown that there is *no significant* difference in the composition of the respective products obtained by the alkylation of isobutane with *s*-butyl fluoride or with 2-butene in the presence of hydrogen fluoride. (Paper presented before the Organic Division of the American Chemical Society at the New York meeting, September, 1944.)

of aluminum chloride monomethanolate) was sealed into the autoclave and 100 cc. (56 g.) of isobutane and 5 g. of hydrogen chloride were pressed in. The stirrer was started and 800 cc. (456 g.) of a mixture of about four parts of isobutane to one of the olefin was added during two to three hours from a charger equipped with a calibrated Jerguson gage. Stirring was continued for an additional one-half hour, after which the autoclave was cooled to room temperature, if necessary, and the gaseous product was slowly led through a soda lime tower into a trap immersed in a Dry Ice–acetone-bath. The autoclave was then cooled to 0° and opened. The liquid product was separated from the catalyst, combined with product from two or three similar experiments, washed and dried. A portion of the washed material was analyzed for chlorine; the remainder was distilled through an 18-inch total reflux fractionation column (wire spiral).[12] The product boiling up to 125° was divided into two parts, one of which was carefully fractionated through a high-temperature Podbielniak column and the various fractions were analyzed[13] by means of their infrared spectra. The other part was used for the octane number determination.

The catalyst was recovered as a dark brown viscous liquid (15–20 g.) when aluminum chloride was used and as a dark brown mixture of crystals and very viscous liquid (15–19 g.) when aluminum chloride monomethanolate was used. The recovery was incomplete owing to difficulty in removing the viscous material from the autoclave; nevertheless, the indications were that more of the hydrocarbon charge was tied up with the catalyst when using the pure aluminum chloride than with the other catalyst.

The alkylates obtained with the aluminum chloride monomethanolate contained unusually large amounts of chlorine (1.0–1.6%) which was present chiefly in the form of *s*-butyl chloride. Its removal from the gasoline, had it been desired, could have been accomplished quite readily by any of several known methods.

No normally liquid product was obtained in an experiment in which a mixture of isobutane and 2-butene was added to a well-stirred mixture of isobutane, hydrogen chloride and aluminum chloride dimethanolate at 72° using the above-described procedure.

Acknowledgment.—The writer wishes to thank Dr. W. S. Gallaway for the analyses of the products by the infrared method and Mr. E. E. Meisinger for assistance in the experimental work.

Summary

1. The respective alkylates obtained by the reaction of isobutane with 1-butene and with 2-butene in the presence of aluminum chloride monomethanolate and hydrogen chloride differed markedly in that the former contained about 60% of dimethylhexanes and 10% of trimethylpentanes whereas the latter contained about 65% of trimethylpentanes and only 4% of dimethylhexanes. A similar difference in composition of the two products was observed when unmodified aluminum chloride was used as catalyst; the alkylation was, however, accompanied by more side reaction.

2. Alkylation of isobutane with propene using aluminum chloride monomethanolate as catalyst yielded a liquid product more than half of which was heptane and consisted of approximately equal amounts of 2,3- and 2,4-dimethylpentane.

3. The mechanism of the alkylation is discussed and the difference in composition of the butene products is explained.

RIVERSIDE, ILLINOIS RECEIVED SEPTEMBER 1, 1945

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[12] C. L. Thomas, H. S. Bloch and J. Hoekstra, *Ind. Eng. Chem., Anal. Ed.*, **10**, 153 (1938).

[13] Analyses by Dr. W. S. Gallaway, Physics Division, Universal Oil Products Company. A description of the analytical method as well as data obtained for the present samples will be given in a paper submitted to the *Analytical Edition of Industrial and Engineering Chemistry.*

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Depolymerization of 3,4,5,5-Tetramethyl-2-hexene and 3,5,5-Trimethyl-2-heptene in Relation to the Dimerization of Isoamylenes[1,2]

BY FRANK C. WHITMORE AND WILLIAM A. MOSHER[3]

The polymerization of the isoamylenes by the action of sulfuric acid gives chiefly the two decenes 3,4,5,5-tetramethyl-2-hexene (V), and 3,5,5-trimethyl-2-heptene (I).[4,5] In acid media both of these olefins may give rise to a carbonium ion[6] containing R_3C—C—C+ by the addition of a proton.[7] Such a carbonium ion has been shown by Whitmore and Stahly[1,8] to split readily giving two smaller olefins. The action of 1-chloro-4-naphthalenesulfonic acid upon the present decenes yielded significant information, especially regarding the formation of 3,4,5,5-tetramethyl-2-hexene which has been recognized as an abnormal polymerization product.[4,5]

Whitmore called attention to the fact that the

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[1] The Polymerization of Olefins. IX. Paper VIII of this series, THIS JOURNAL, **67**, 2168 (1945).

[2] From a part of the dissertation submitted by W. A. Mosher in partial fulfillment of the degree of Doctor of Philosophy, The Pennsylvania State College, 1940.

[3] The Eastman Kodak Co. Research Fellow in Chemistry, 1939–1940. Present address: University of Delaware, Newark, Delaware.

[4] Drake, Kline and Rose, THIS JOURNAL, **56**, 2076 (1934).

[5] Whitmore and Mosher, *ibid.*, **63**, 1120 (1941).

[6] The term "carbonium ion" is used in the sense employed by L. P. Hammett in "Physical Organic Chemistry," McGraw-Hill Company, 1940, but with the reservations stipulated by the present senior author in reference 7. The "+" sign is used in place of the "*" previously employed to indicate the carbon atom having only a sextet of electrons, this electronic deficiency being due usually to the decomposition of an oxonium compound or to the addition of a proton or other electrophyllic group or compound to a multiple linkage but rarely to a simple ionization such as that of the trityl halides in liquid sulfur dioxide.

[7] Whitmore, THIS JOURNAL, **54**, 3274 (1932).

[8] Whitmore and Stahly, *ibid.*, **55**, 4153 (1933).