with ether, the combined liquids were filtered and the solvents were evaporated. The residue, crystallized from dilute ethanol, melted at 84–87°, and weighed 10.75 g. (88%). Several crystallizations from dilute ethanol gave a product which melted at 89–90.5°.

Anal. Calcd. for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 83.31; H, 7.16.

2,3-Dimethyl-5-benzhydrylhydroquinone (**XIX**).—A mixture of the dimethyl ether XVIII (4.78 g.), hydrobromic acid (48 cc., 48%), and acetic acid (66 cc.) was refluxed for two and one-half hours. The dark solution was poured into water, and the solid was removed and crystallized from benzene–petroleum ether (b. p. 30–60°) (Norit). The product (2.74 g., 63%) melted at 139–141°. A sample, recrystallized several times, melted at 142–143°.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 83.15; H, 6.40.

Cleavage of the ether XVIII by action of hydriodic acid in acetic acid gave XIX in only 19% yield, in contrast with the excellent yield of XVI obtained from XIV by means of this procedure. Use of 40% hydrobromic acid in acetic acid also gave poor results (19%) when applied to the cleavage of XVIII. The hydroquinone XIX could not be condensed with isoprene hydrobromide or with isoprene. Four attempts were made to carry out the condensation with the hydrobromide; three in ligroin, and one in acetic acid. Condensation with isoprene was attempted twice, but no chroman was formed.

2,3-Dimethyl-5-benzhydrylhydroquinone Diacetate (**XX**).—Sulfuric acid (1 drop) was added to a solution of the hydroquinone XIX (120 mg.) in acetic anhydride (5 cc.). After standing for three minutes, the solution was poured into water. The solid was removed and crystallized three times from benzene–petroleum ether (b. p. 30–60°); it then melted at 185.5–186.5°.

Anal. Calcd. for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23. Found: C, 77.15; H, 6.41.

Summary

1. 2,2,7,8-Tetramethyl-5-benzyl-6-hydroxychroman (II) has been prepared from 2,3-dimethylnitrobenzene.

2. This chroman has been oxidized, by action of silver nitrate, to the yellow *p*-benzoquinone V. Vigorous oxidation of the chroman by action of silver nitrate in ethanol, or of nitric acid in the same solvent, produced red solutions but none of the red *o*-quinone VI could be isolated from these solutions.

3. Oxidation of the yellow *p*-benzoquinone V by action of silver nitrate in ethanol or of nitric acid in the same solvent did not produce the red *o*-quinone VI—indeed, did not even produce red solutions. The *p*-quinone V, therefore, is not an intermediate in the production of the red solutions by oxidation of the chroman II.

4. The only evidence obtained for the existence of a tautomeric form of the yellow *p*-quinone V was its solubility in Claisen alkali.

5. Several intermediates, leading to 2,2,7,8-tetramethyl-5-benzhydryl-6-hydroxychroman III have been prepared, but the chroman itself could not be prepared because the corresponding hydroquinone could not be condensed with isoprene or isoprene hydrobromide.

6. The results of this work have necessitated some modifications of previous statements with regard to the oxidative behavior toward silver salts and nitric acid of *p*-hydroxychromans related to the tocopherols. The oxidation always leads to yellow *p*-quinones, but the only known cases in which red *o*-quinones are formed (in amounts sufficient to isolate), with elimination of the group originally present in the 5-position of the chroman, are those in which this group is hydrogen or methyl. A benzyl group in this position is certainly not eliminated; likewise, another chroman ring attached in the 5-position is not eliminated.[1a] Finally, some evidence has appeared that the red *o*-quinones, when they are formed, may be produced directly from the *p*-hydroxychromans, and not via the yellow *p*-quinones as intermediates.

MINNEAPOLIS 14, MINNESOTA RECEIVED JUNE 2, 1944

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Exchanges of Halogen and Hydrogen between Organic Halides and Isoparaffins in the Presence of Aluminum Halides

BY PAUL D. BARTLETT, FRANCIS E. CONDON[1] AND ABRAHAM SCHNEIDER[1]

Introduction.—The experiments reported in this paper constitute part of a study of the mechanism of low-temperature paraffin alkylation. This reaction presents at the outset a mechanistic paradox. One of the strongest catalysts is aluminum chloride, which is known to be a powerful polar reagent and electron acceptor. On the other hand, the isoparaffin which is induced to react is the extreme of a non-polar and non-ionizing compound. The problem is whether the attack of a polar catalyst upon this system can have anything in common with the usual function of this catalyst in many other organic reactions whose mechanisms are known.

Little progress has been made in resolving the complex alkylation reaction into successive steps, under the conditions of its commercial use. Usually if the reaction is interrupted at an early stage, it is found that some of the reactants have been converted into a rather complex mixture of products, while the rest remain unchanged. To circumvent this difficulty we selected for study the alkylation of isopentane with *t*-butyl chloride, catalyzed by aluminum bromide, since both aluminum bromide and *t*-butyl chloride are soluble

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[1] Universal Oil Products Co. Fellows 1941–1944.

in isopentane and diffusion to or from an interface was expected to play no part in determining the course of the reaction. Actually, two liquid phases appear when solutions of aluminum bromide and of *t*-butyl chloride in isopentane are mixed, so that the homogeneity of this system is short-lived.

Isopentane and *t*-Butyl Chloride.—When reaction was brought about between isopentane, *t*-butyl chloride, and aluminum bromide in excess of the hydrocarbon as solvent, at or slightly below room temperature, a complex product was obtained whose distillation curve (Fig. 1, Curve 3) resembled that of a typical paraffin alkylate. To arrest this reaction at an early stage it was necessary to devise a flow system (Fig. 2) whereby the reactants could be mixed for very short times of contact and the reaction then quenched by addition of water or an alkali solution. The two solutions to be mixed were made up in isopentane as a solvent: one containing aluminum bromide and the other containing *t*-butyl chloride. These solutions were forced by a common head of compressed air out of the twin reservoirs A at rates controlled by the stopcocks B, into the nozzle C, where mixing occurred. C fitted into a section D, at the end of which the reacting solution met a rapid stream of water which inactivated the aluminum bromide and quenched the reaction. In the first trial the concentrations were such that equal volumes of the two solutions contained equimolar amounts of *t*-butyl chloride and aluminum bromide. Later it was found that a full molar equivalent of aluminum bromide was not needed, and that the results were the same using a smaller quantity of this compound.

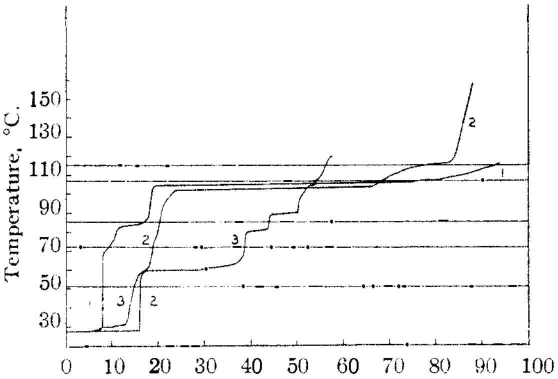


Fig. 1.—Distillation of the product of reaction between isopentane and *t*-butyl chloride with aluminum bromide at room temperature: Curve 1, 3 *t*-BuCl : 1 $AlBr_3$; contact time ~0.001 sec.; Curve 2, 1 *t*-BuCl : 1 $AlBr_3$; contact time ~1 sec.; Curve 3, 1 *t*-BuCl : 1 $AlBr_3$; contact time ~20 min. Horizontal lines mark boiling points of *t*-BuCl, *t*-BuBr, *t*-AmCl, *t*-AmBr, and 2-Me-3-Br-butane.

The duration of effective contact between the reactants in this apparatus can be estimated only roughly because of the finite time required for the initial mixing of the reactants and for the quenching with water. A qualitative estimate of the time can be made by assuming that both mixings are practically instantaneous. Then

$$\text{“Duration of contact”} = (\text{Total time of experiment}) \frac{(\text{Volume of D})}{(\text{Total volume of reacting solution})}$$

The mixing chamber D had a volume of 0.65 cc. In a typical run it required 478 seconds to empty 1400 cc. of liquid from the two reservoirs. The approximate reaction time is therefore 0.22 second. Two modifications of this apparatus were used in other experiments: the one, an earlier slower form, in which the mixed hydrocarbon solutions were fed onto the shaft of a stirrer and thus introduced into the quenching bath; and the other in which the mixing chamber D was eliminated and the nozzle immersed directly in the vigorously stirred quenching bath. The estimated reaction times in these two modifications were 1 sec. and 0.001 sec., respectively.

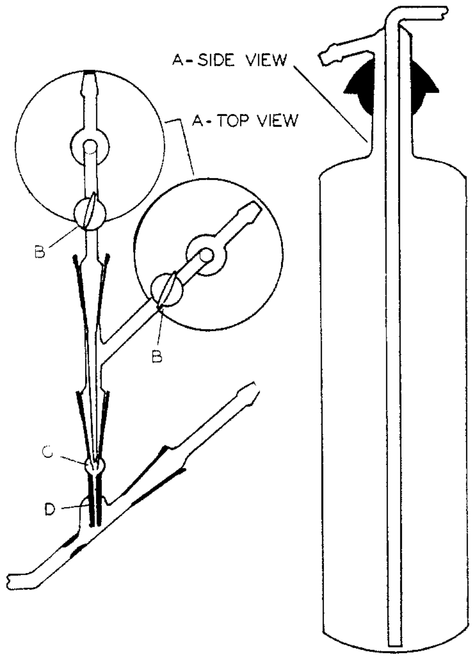


Fig. 2.

The hydrocarbon layer in each experiment was separated from the quenching bath, washed with water and carbonate solution, dried and distilled. Curves 1 and 2 in Fig. 1 show the results after 0.001 and 1 sec., respectively. In each case the principal product was *t-amyl bromide*, accompanied by a smaller amount of 2-methyl-3-bromobutane. These compounds were both identified by the preparation of solid derivatives and mixed melting points. The latter compound was shown to be formed to the extent of about 20% when *t*-amyl bromide was allowed to stand with aluminum bromide. In later runs, in which *t*-amyl chloride and a higher isoparaffin were used, iso-

TABLE I

HALIDES PRODUCED FROM THE PARENT HYDROCARBONS BY *t*-BUTYL CHLORIDE AND ALUMINUM CHLORIDE OR ALUMINUM BROMIDE

Halide	Yield, %	Identified by derivative	Melting point, °C.
t-Amyl bromide	50–70	α,α-Dimethylbutyranilide	90–92[a]
2-Bromo-3-methylbutane[b]	10–15	Methylisopropylcarbinyl 3,5-dinitrobenzoate	73–75[a]
2-Chloro-2,3-dimethylbutane	23	Carboxylic acid amide Olefin dibromide *p*-Hexylphenol	125–127 173–174 103–104
3-Chloro-2,2,3-trimethylbutane	16	Itself a solid	128–133[a]
1-Chloro-1-methylcyclohexane	30	1-Methylcyclohexanol Phenylurethan Furoic acid derivative	 104–105 112–113
9-Chlorodecahydronaphthalene	50.5 (Combined yield)	Blue nitrosochloride from olefin	90.5–91.5
1-Chlorodecahydronaphthalene		*trans*-α-Decalone-2,4-dinitrophenylhydrazone	222–223

[a] Mixed melting point. [b] From *t*-amyl bromide.

pentane was identified as a product of the reaction.

From these results it is evident that the first recognizable reaction between isopentane and *t*-butyl chloride with aluminum bromide is an extremely rapid *halogen–hydrogen exchange* in which the original paraffin is converted into halide and the original halide into paraffin

$$(CH_3)_3CCl + C_2H_5(CH_3)_2CH \xrightarrow{AlBr_3} (CH_3)_3CH + C_2H_5(CH_3)_2CBr$$

The completeness of this reaction is shown by the total absence of any *t*-butyl chloride even in the product of the "0.001 second" reaction and by the isolation of *t*-amyl bromide in 50–70% yields. The conditions favor some loss of this bromide by hydrolysis during quenching. The boiling point of *t*-butyl chloride is marked by the lowest horizontal line on the graph. In the 1-second run, in which equimolar amounts of *t*-butyl chloride and aluminum bromide were used, there is no evidence of any organic chloride but only the two amyl bromides. In the "0.001-second" and "0.22-second" runs, using *t*-butyl chloride and aluminum bromide in a mole-ratio of 3 to 1, the product in each case contains a small amount of *t*-amyl chloride in addition to the bromide. All experiments were conducted at least in duplicate. The curve for the "0.22-second" reaction product is not shown, since it is practically identical with the product from the "0.001-second" run.

From a comparison of Curves 1 and 2 of Fig. 1, three things are seen to have occurred between 0.001 sec. and 1 sec. in this system: (1) a slight amount of *t*-butyl bromide, present earlier, has disappeared. It seems possible that if the reaction time could be cut a further power of ten, chloride-bromide exchange within the *t*-butyl chloride would be found the fastest reaction of all. (2) Isomerization of *t*-amyl bromide partially into 2-bromo-3-methylbutane has occurred. (3) A slight inflection in Curve 2 near 60° is the first indication of a low-boiling alkylation product. It is either 2,3-dimethylbutane or 2-methylpentane, both "abnormal" products (see below). It is to be noted, however, that there is a quite appreciable amount of high-boiling alkylate to be found in this product. Curve 3, included in the figure for comparison, shows the composition of a similar mixture after standing for a number of minutes.

Isopentane and Isopropyl Chloride.—Under the same conditions isopropyl chloride and aluminum bromide also lead to the formation of *t*-amyl bromide from isopentane, and in yields similar to those from the *t*-butyl chloride.

Halogen–Hydrogen Exchanges Involving Paraffins Other than Isopentane.—Although aluminum chloride is not soluble in paraffins as is aluminum bromide, the chloride can also be used to effect halogen–hydrogen exchanges. The yields are lower in this case. Table I shows some of the exchange reactions which have been carried out, using either aluminum bromide or aluminum chloride. The yields do not represent maxima, since in many cases optimal conditions were not worked out. No halogen–hydrogen exchange occurred when *n*-pentane was substituted for the isopentane. Poorly characterized products were obtained with hydrindane, cholestane, camphane and bicyclo[2,2,1]heptane.

Attempted Halogen–Hydrogen Exchanges with 2,2,4-Trimethylpentane.—Treatment of 2,2,4-trimethylpentane with *t*-butyl chloride and aluminum chloride under the same conditions which led to the products of Table I failed to yield the expected chlorination product of the isoöctane. Halogen–hydrogen exchange occurred, however, in the opposite direction; 2,2,4-trimethyl-4-chloropentane (diisobutylene hydrochloride) was treated with isopentane (more convenient than isobutane because of boiling point) and aluminum chloride, with the production of 9% of the possible *t*-amyl chloride. At the same time a complex mixture was obtained whose chief recognizable components were 2,2,4-trimethylpentane (in amount equivalent to the *t*-amyl chloride) and a mixture of nonyl chlorides whose identification remains incomplete.

The Mechanism of the Halogen-Hydrogen Exchange.—It seems important in seeking to discover the mechanism of a catalytic process that a role should be assigned to the catalyst which is in conformity with its known chemical character. The aluminum halides are, first and foremost, electron acceptors, and in the present system it seems most probable that the aluminum atom completes its octet of electrons by attaching itself firmly to the chlorine atom of the *t*-butyl chloride, thus giving a complex in which there is an actual or virtual *t*-butyl positive ion. The behavior of such a molecular species in an aqueous or alcoholic medium is well known,[2,3] but studies of it in a hydrocarbon solution are lacking. We suggest that in isopentane the *t*-butyl positive ion is capable of stripping off a hydrogen—in this case a tertiary one—with its pair of bonding electrons, thus saturating the *t*-butyl fragment as isobutane and leaving a *t*-amyl positive ion in its place. On isolation of the product this appears as a halide, the halogen coming from reunion with

$$(CH_3)_3CCl + AlCl_3 \rightleftarrows (CH_3)_3C^+\ AlCl_4^-$$

$$(CH_3)_3C^+ + C_2H_5(CH_3)_2CH \rightleftarrows (CH_3)_3CH + C_2H_5C(CH_3)_2^+$$

$$C_2H_5C(CH_3)_2^+ + AlCl_4^- \rightleftarrows C_2H_5C(CH_3)_2Cl + AlCl_3$$

the AlX_4^- ion. Thus it is that the identity of the organic halogen is changed from chlorine to bromine during the exchange with aluminum bromide as catalyst. This process is analogous to an intramolecular rearrangement in which hydrogen migrates with its bonding pair of electrons from one carbon atom to an adjacent one carrying an open sextet.[2a] The only difference is that in the reaction now visualized the shift of the "hydride" particle occurs at a collision between two different molecules.

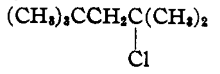
Possible Relationship of Halogen-Hydrogen Exchange to the Mechanism of Alkylation.[3a]—The fact that halogen-hydrogen exchange occurs under alkylating conditions does not, of course, prove that it plays any essential part in the alkylation process. On the other hand, it does make it possible to describe isoparaffin alkylation as a succession of steps, the like of which can be shown actually to occur under the conditions in question, and about which there is some existing body of knowledge and rational theory. Such a description, in abbreviated terms, has been given by Schmerling[4] for the alkylation of isobutane with ethylene in the presence of aluminum chloride to yield 2,3-dimethylbutane. Schmerling's mechanism is in accord with the facts presented in this paper and, as expanded and supplemented below, can serve as a general mechanism for the alkylation of isoparaffins by olefins or alkyl halides in the presence of aluminum halides. For simplicity's sake let us consider the alkylation of isobutane with *t*-butyl chloride and aluminum chloride and divide the discussion into that of the "normal" products (those having a multiple of four carbon atoms) and the "abnormal" products (those having a number of carbon atoms not a multiple of four).

The "Normal" Products.—The "normal" products can be accounted for by the following sequence of reactions which are individually well known.

1. Reversible elimination of halogen acid

$$(CH_3)_3CCl \overset{AlCl_3}{\rightleftarrows} HCl + (CH_3)_2C{=}CH_2$$

2. Addition of halide to olefin



$$(CH_3)_3CCl + CH_2{=}C(CH_3)_2 \overset{AlCl_3}{\rightleftarrows} (CH_3)_3CCH_2\underset{\displaystyle Cl}{\underset{|}{C}}(CH_3)_2 \quad (I)$$

3. Halogen-hydrogen exchange

$$\underset{(I)}{(CH_3)_3CCH_2C(CH_3)_2Cl} + (CH_3)_3CH \overset{AlCl_3}{\rightleftarrows} (CH_3)_3CCl + (CH_3)_3CCH_2CH(CH_3)_2 \text{ (2,2,4-trimethylpentane)(II)}$$

4. Partial isomerization (analogous to that observed with *t*-amyl bromide and aluminum bromide)

$$\underset{(I)}{(CH_3)_3CCH_2C(CH_3)_2Cl} \overset{AlCl_3}{\rightleftarrows} \underset{(III)}{(CH_3)_3CCHClCH)(CH_3)_2}$$

5. Wagner-Meerwein rearrangement[5]

$$\underset{(III)}{(CH_3)_3CCHClCH(CH_3)_2} \overset{AlCl_3}{\rightleftarrows} \underset{(IV)}{(CH_3)_2CClCH(CH_3)CH(CH_3)_2}$$

From this product Reaction 3 gives some 2,3,4-trimethylpentane (V), another of the normal products. This isoparaffin, in turn, is subject to further halogen-hydrogen exchanges and isomerization from which 2,3,3- and 2,2,3-trimethylpentanes can be derived strictly in accordance with demonstrated analogy.[6]

The unity of the foregoing scheme becomes more apparent when the reactions are discussed in terms of their probable mechanisms, for the carbonium ion, or active fragment with an electron-deficient carbon atom,[7] is the key species in all these processes.[5]

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[2] Whitmore, (a) THIS JOURNAL, **54**, 3274-3283 (1932); (b) *Ind. Eng. Chem.*, **26**, 94 (1934).

[3] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, Chapter 10.

[3a] For previous theories of the mechanism of low-temperature alkylation see Ipatieff and Grosse, THIS JOURNAL, **57**, 1616 (1935); Caesar and Francis, *Ind. Eng. Chem.*, **33**, 1426 (1941); McAllister, Anderson, Ballard and Ross, *J. Org. Chem.*, **6**, 647 (1941).

[4] L. Schmerling, private communication, November 21, 1942; THIS JOURNAL, **66**, 1422 (1944).

[5] Compare (a) Laughlin, Nash and Whitmore, THIS JOURNAL, **56**, 1395 (1934); (b) Whitmore and Johnston, *ibid.*, **60**, 2265 (1938).

[6] Compare references 2, 3, 5.

[7] We prefer for the present to leave open the question of whether the lifetime of the intermediate is such as to justify the use of the term "ion."

Reaction 1 becomes a very rapid equilibrium in the presence of aluminum halides because of the highly ionic complexes formed between these and organic halides

$$(CH_3)_3CCl + AlCl_3 \rightleftarrows (CH_3)_3C^+ \, AlCl_4^- \rightleftarrows (CH_3)_2C{=}CH_2 + H^+ \, AlCl_4^-$$

The polymerization of isobutylene is best described in terms of carbonium ions.[8] If Reaction 2 proceeds by way of an ionic complex as postulated, the attack of the carbonium ion upon the olefin would be expected to follow the same course as in the ionic mechanism of polymerization. The reaction, of course, need not stop with the dimer in either case, but since these reactions are reversible it is possible to obtain considerable amounts of transformation products of any polymer which is subject to any sort of further reaction.

Reaction 3 represents an example of halogen–hydrogen exchange which, when studied separately, proceeded with poor yield. This is probably because of the great ease with which diisobutylene hydrochloride undergoes isomerization, rearrangement, and depolymerization in the presence of aluminum halides under our experimental conditions. At least the reality of Reaction 3 has been shown, and it may account for the small amount of 2,2,4-trimethylpentane actually found in alkylation under these same conditions.

Reaction 4 can be represented as an elimination and readdition of halogen acid in partial opposition to Markownikoff's rule. In our simplest isolated case of such a reaction it was found that *t*-amyl bromide, on treatment with aluminum bromide, always went into an equilibrium containing 15–20% of 2-methyl-3-bromobutane. This is a simple illustration of the recognized fact that Markownikoff's rule is a generalization applying to the *major product* only. This example makes it appear reasonable that any tertiary halide, in the presence of an appropriate catalyst, should yield appreciable quantities—as much as 20%—of any secondary halides derivable by simple elimination and readdition of halogen acid. Although this reaction can be described in these terms, it is not at all certain that a proton needs to leave the carbonium ion in order to bring about the isomerization. It would be in accord with existing theory[2a] to postulate a reversible rearrangement in the carbonium ion

$$(CH_3)_3CCH_2C^+(CH_3)_2 \rightleftarrows (CH_3)_3CC^+HCH(CH_3)_2$$

which involves the direct shift of a hydrogen atom with its electron pair from one carbon to the next.[5b] In any case, the inclusion of Reaction 4 in our mechanism requires no special justification, since the occurrence of such partial isomerizations has been experimentally established.

Now although the equilibrium between I and III is undoubtedly in favor of the former, III can do something not possible for I. Being a halide of the "pinacolyl" type, III can and will undergo rapid and practically irreversible isomerization in the sense of the Wagner–Meerwein rearrangement (Reaction 5). Such a reaction ensues inevitably when a secondary halide with a completely substituted β-carbon atom exists in the presence of an aluminum halide.[5b] The removal of III by rearrangement will constantly displace the equilibrium I $\rightleftarrows$ III so that a balance of competing rates of reaction will determine the relative resulting amounts of 2,2,4-trimethylpentane and hydrocarbons derived from rearrangement products, such as 2,3,4-trimethylpentane.

Nenitzescu and his co-workers[9] have observed the reduction of alkyl, acyl and certain inorganic halides by reaction with aluminum chloride and such hydrocarbons as would yield branched isomers under the conditions used. The results of these workers can be well described in terms of the reaction mechanism here presented.

The "Abnormal" Products.—The "abnormal" products of five, six, seven, etc., carbon atoms might be formed by direct transfer of an alkyl group (presumably with its pair of bonding electons) from one hydrocarbon molecule to another, or by cleavage of a larger molecule into fragments. The former possibility has not been either demonstrated or excluded. On the basis of the latter alone, however, it is possible to account for some of the prevalent "abnormal" or odd-carbon products of alkylation reactions. Those low polymers which are readily formed by ionic mechanisms are also readily depolymerized under the same conditions. The criterion for ready cleavage of any carbonium ion is the possibility of forming a relatively stable smaller carbonium ion by cleavage between carbon atoms 2 and 3 (numbering from the carbon atom bearing the positive charge).[10] Thus diisobutylene is readily depolymerized through the ionic cleavage

$$(CH_3)_3CCH_2C(CH_3)_2^+ \rightleftarrows (CH_3)_3C^+ + CH_2{=}C(CH_3)_2$$

because the smaller carbonium fragment produced is *tertiary* and as stable as the first. The fragments produced in this way are likely to be the same as those from which the low polymer was formed unless a rearrangement intervenes between the polymerization and the cleavage. Such a rearrangement does occur in the formation of 2,3,4-trimethylpentane (V) and its precursor, the chloride IV, in the scheme above. The carbonium ion from IV could undergo the cleavage

$$(CH_3)_2CHCH(CH_3)C(CH_3)_2^+ \longrightarrow \underset{\text{VI}}{(CH_3)_2CH^+} + \underset{\text{VII}}{CH_3CH{=}C(CH_3)_2}$$

VI is an isopropyl positive fragment which would promptly attach itself to an isobutene molecule yielding 2,4-dimethylpentene-1 and, by addition of hydrochloric acid and halogen–hydrogen exchange, 2,4-dimethylpentane. The trimethyl-

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(8) Reference 2b; Ref. 3, pp. 292 and 307.

(9) Nenitzescu and Ionescu, *Ann.*, **491**, 189–210 (1931); Nenitzescu and Dragan, *Ber.*, **66**, 1892 (1933); Nenitzescu and Isacescu, *ibid.*, **67**, 1391 (1934).

(10) Whitmore and Stahly, THIS JOURNAL, **55**, 4153 (1933).

ethylene, VII, could undergo polymerization, copolymerization, or reactions 1 and 3 yielding the isopentane which commonly accompanies the alkylation of isobutane with isobutene. Although the possibilities of such depolymerizations of octanes are limited, they increase greatly when the scheme is extended to higher polymers of isobutene, and since tri- and tetraisobutylenes are subject to the same principles as diisobutylene, it is fairly sure that such rearrangements and cleavages of higher polymers go on, whether or not they are critical in determining the chief reaction products.

The Effect of Time in the Alkylation of Isopentane with Isobutene.—The evidence presented in Fig. 3 is consistent with the view that the formation of an olefin polymer is an intermediate step in low-temperature alkylation by an olefin and aluminum chloride. When the reaction between isobutylene, isopentane and aluminum bromide was carried out in our flow apparatus with a reaction time of about 0.22 second, the product consisted largely of high polymers. It was distilled at successively lower pressures until, at 3 mm. and with a bath temperature of 320°, distillation ceased. Curve 1 of Fig. 3 is a schematic curve showing this distillation corrected to 760 mm. pressure for comparison with Curve 2. Curve 2 represents the distillation of the product in a similar reaction allowed to run for the much longer time of one and three quarters hours. It is seen to be a typical alkylate, and indeed very similar in character to the late product from the reaction between *t*-butyl chloride, isopentane, and aluminum bromide (Curve 3 of Fig. 1). Although the polymerization of isobutylene is reversible, these observations lend some support to the idea that the alkylate consists largely of cleavage products of polyisobutylenes.

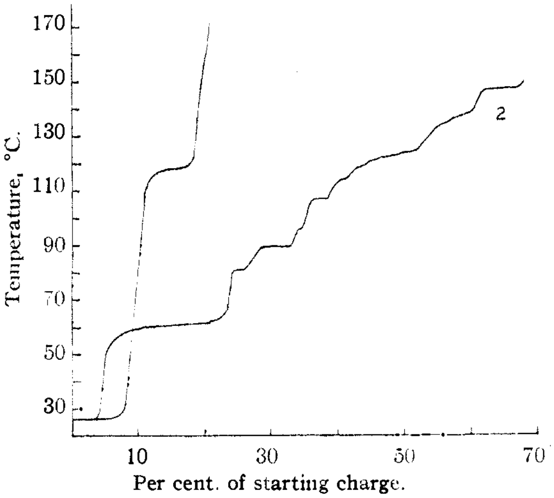

Fig. 3.—Distillation of product of reaction between isopentane and isobutylene with aluminum bromide: Curve 1, 12 isobutylene:1 $AlBr_3$; contact time ~0.2 sec. (precooled to 0°); Curve 2, 4 isobutylene:1 $AlBr_3$; contact time 105 minutes (at room temperature).

In any aluminum halide alkylation, if the isoparaffin and the olefin or the isoparaffin and the organic halide, do not have the same skeletal structure, then the way lies open for a rapid equilibration (by the halogen-hydrogen exchange) whereby both possible paraffins, and both possible olefins or halides, are produced in proportions determined by their natures and the conditions of the experiment.

Self-Saturation of Olefins.—If our proposed mechanism for halogen-hydrogen exchange is correct, then the point of attack on the paraffin must be determined to a large extent by the ease of formation of the resulting carbonium ion. It would be predicted that not only tertiary alkyl ions but also ions of the allyl type, because of their stabilizing resonance, would be readily formed in such a system as this. Whenever an olefin and an aluminum halide are present with a trace of hydrogen halide some hydrogenation and dehydrogenation should occur according to the scheme,

$$RCH_2CH_2CH{=\!=}CHR' + HX + AlX_3 \rightleftarrows RCH_2CH_2C^+HCH_2R' + AlX_4^-$$

$$RCH_2CH_2C^+HCH_2R' + RCH_2CH_2CH{=\!=}CHR' \rightleftarrows RCH_2CH_2CH_2CH_2R' + RCH_2C^+HCH{=\!=}CHR$$

$$RCH_2C^+HCH{=\!=}CHR' + AlX_4^- \rightleftarrows RCH{=\!=}CHCH{=\!=}CHR' + HX + AlX_3$$

If the olefin concerned is of high molecular weight, a long conjugated system will be built up. Because the formation of conjugated from unconjugated systems involves a stabilization of about 3–4 kilocalories for each double bond transferred into conjugation,[11] the final result of this process should be the formation of highly unsaturated residues and saturated hydrocarbons. Such a result is often observed in the polymerization of olefins by aluminum chloride.[12]

Experimental

Materials.—Isopentane was obtained from the Phillips Petroleum Co., being of technical grade. It was purified by distillation through a 45-plate column with Lecky–Ewell spiral screen packing at a reflux ratio of 50 to 1. The isopentane used boiled constantly at 27.8° and had $n^{21.6}_{4}$ 1.3528.

The 2,3-dimethylbutane used was furnished by the Universal Oil Products Co. It boiled at 58–59°.

2,2,3-Trimethylbutane (triptane) was prepared according to the directions of Wibaut and co-workers,[13] the final hydrogenation being conducted with Raney nickel at 120° and 1000 lb. pressure. The material used boiled at 80°, n^{20}_{D} 1.389.

Isopropylcyclohexane was prepared by the hydrogenation of cumene over Raney nickel. It boiled at 154–155°, n^{25}_{D} 1.4386. The removal of unchanged cumene was troublesome and was finally accomplished by nitration followed by distillation.

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[11] Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **58**, 146 (1936).

[12] C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, p. 798.

[13] Wibaut, Hoog, Langedijk, Overhoff and Smittenberg, *Rec. trav. chim.*, **58**, 347 (1939).

2,2,4-Trimethylpentane (isoöctane) was the best grade of Rohm and Haas, having b. p. 99.2°.

Methylcyclohexane was purchased from the Barrett Co. It was redistilled, the portion used boiling at 100° constantly.

Decalin from the Eastman Kodak Co. was shaken three times with concentrated sulfuric acid, washed with water and potassium carbonate solution, dried and distilled. At 24 mm. the liquid boiled at 81–83°.

Aluminum chloride used was Mallinckrodt "Analytical Reagent" grade.

Aluminum bromide was prepared using an apparatus similar to that described by Winter and Cramer.[14] A 500-cc. reaction flask was used.

Distillations.—The distillation of all halogen-containing products was carried out in a 1-m. × 11-mm. column packed with single turn glass helices,[15] except where otherwise noted. In the exploratory runs metal packing was used and continuous decomposition of the halides occurred during distillation, necessitating the change to glass packing.

Procedure for Halogen-Hydrogen Exchanges.—When aluminum chloride was the catalyst the reactants were shaken together in a separatory funnel for several minutes, then the catalyst separated and the organic liquid washed with water, dried with potassium carbonate, and distilled. When aluminum bromide was used there were two procedures. For obtaining the shortest contact times the apparatus of Fig. 2 was employed, the reacting solutions flowing together and the reaction being immediately quenched by vigorous stirring with water. Where contact of ten seconds or longer was desired the solutions of *t*-butyl chloride and of aluminum bromide in the paraffin were mixed and water then added as soon as homogeneity had been established.

Identification of halides was preferably accomplished by the formation of a Grignard reagent and the reaction of this with phenyl or naphthyl isocyanate to yield a crystalline anilide or naphthalide. This was successful only in the cases of *t*-butyl chloride, *t*-amyl chloride and bromide. Other methods employed included: (1) carbonation of the Grignard reagent and use of either the carboxylic acid or its amide as the characterizing derivative, (2) elimination of halogen acid from the halide and characterization of the resulting olefin through a nitrosochloride or dibromide, (3) hydrolysis of the halide to an alcohol and preparation of a urethan or 3,5-dinitrobenzoate, (4) reaction of the halide with phenol or furoic acid to yield a solid derivative, (5) oxidation of the Grignard reagent to the alcohol, oxidation to a ketone, and preparation of ketone derivatives (used for 1-chlorodecalin). The details follow of some of the identifications of halides.

Products from 2,3-Dimethylbutane.—The product from 100 g. of the paraffin and 53.6 g. of *t*-butyl chloride shaken with 10 g. of aluminum chloride for one-half minute distilled as follows, using a modified Claisen flask

°C.	G.	°C.	G.
28–55	21.0	65–108	13.6
55–58	30.5	108–114	23.5
58–65	7.0	Residue	8.2

Redistillation of the last volatile fraction gave 16.23 g. boiling at 68° under 185 mm. pressure, or a 23% yield. Heating 5 g. of this chloride with 5 g. of phenol at 100° for three hours gave a distillable oil which crystallized after two months, melting (after recrystallization from ligroin) at 103–104°. *p*-2,3-Dimethyl-2-butylphenol is reported to melt at 105–106°.[16] Other derivatives obtained were the amide of the carbonation product of the Grignard reagent, m. p. 125–127° (reported, 128°)[17] and tetramethylethylene dibromide, m. p. 173–174° cor. (reported, 168°).[18]

Product from Triptane.—The product of thirty to forty-five seconds of shaking of 55 g. of 2,2,3-trimethylbutane and 28 g. of *t*-butyl chloride with 6 g. of aluminum chloride was washed, dried, and distilled through a modified Claisen flask. The fractions were as follows

°C.	G.	n^{20}_D
to 65	16	1.3816
65–71	15	1.3856
71–75	9	1.3876
75–85	16	1.3902

Much gas evolution accompanied the first fraction. The residue crystallized on standing in the refrigerator, the crude solid weighing 6.5 g. After recrystallization from ether it melted at 128–133° and gave a slow test for halogen with alcoholic silver nitrate. An authentic specimen of the chloride from pentamethylethanol melted at 133°; mixed melting point, 133°.

Preparation of 2,2,3-Trimethyl-3-chlorobutane as a Reference Compound.—This compound was prepared by treating 10 g. of pentamethylethanol with acetyl chloride until there was no more reaction. The mixture was poured into water, the solid filtered off and crystallized from ether. The yield was 5 g. (46%) of material melting at 133°.

Attempted Chlorine–Hydrogen Exchange between 2,2,4-Trimethylpentane and *t*-Butyl Chloride.—A solution of 50 g. (0.438 mole) of isoöctane and 20 g. of *t*-butyl chloride was shaken with 5 g. of aluminum chloride for one-half minute. There was little evidence of reaction. When the reaction was quenched and the product worked up as usual, the distillation at 760 mm. resulted in the following fractions

°C.	G.
31–51	2.1
51–70	3.39
70–99	23.33
99–103	23.58

Chlorine–Hydrogen Exchange between Isopentane and Diisobutylene Hydrochloride.—Fifty grams (0.338 mole) of diisobutylene hydrochloride, b. p. (40 mm.) 62.8°, n^{24}_D 1.4286, dissolved in 100 g. (1.39 moles) of isopentane was shaken with 5 g. of aluminum chloride for two minutes before quenching. On working up, the material was first roughly separated into two fractions and these were separately distilled through a 2-foot Podbielniak spiral column. The original 25 g. boiling from 40–102° was separated into three fractions at atmospheric pressure

	°C.	G.	n^{20}_D
1	30–85	9.57	....
2	86–88	6.07	1.3985
3	89–98	4.93	1.3970

Fraction 2 was identified as *t*-amyl chloride by means of the anilide of the related hexanoic acid, m. p. 91–92° (mixed m. p. 90.5–92°).

The higher-boiling material from the original crude separation was distilled at 29 mm. through the same 2-foot Podbielniak column

	°C.	G.	n^{19}_D
4	37–52	14.53	1.4123
5	52–60	6.97	1.4296
6	60–64	19.15	1.4346
7	64–87	6.72	1.4362
8	87–103	2.25	1.4400
Residue		16.69	

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[14] Winter and Cramer, *Ind. Eng. Chem.*, **32**, 856 (1940).

[15] Wilson, Parker and Laughlin, This Journal, **55**, 2795 (1933).

[16] Huston and Hsieh, *ibid.*, **58**, 439 (1936).

[17] Whitmore and Laughlin, *ibid.*, **55**, 3735 (1933).

[18] Grosse and Ipatieff, *J. Org. Chem.*, **8**, 441 (1943).

Fraction 5 has the properties of diisobutylene hydrochloride. It is evident that conversion of this into other products is very rapid, as was postulated in the preceding discussion of the mechanism of alkylation.

Reaction between Isopentane and *t*-Amyl Bromide with Aluminum Bromide.—This experiment was carried out in the flow apparatus, but with an additional coil of 29 turns of 2-mm. glass tubing introduced between D and E. The duration of reaction was computed to be about ten seconds. The two solutions flowing together contained, respectively, 80 g. of aluminum bromide (0.30 mole) in 297 g. of isopentane and 136 g. (0.90 mole) of *t*-amyl bromide in 234 cc. of isopentane. The reaction was carried out at 20°. Of the original 667 g. of organic material, 626 g. was recovered after the water washing, dried with potassium carbonate, and reduced to 158 g. by removal of the isopentane through a short Widmer column. In all, 137 g. boiled above 28°, as follows

°C.	G.	
59–63	4	2,3-Dimethylbutane or 2-methylpentane
63–103	11	Unresolved
103–106	64	*t*-Amyl bromide
106–112	6	
112–118	16	2-Bromo-3-methylbutane
118–153	11.5	
Residue	8	
Hold-up	8	
Loss	8.5	

The chief point of interest in this run is the isomerization of *t*-amyl bromide into 2-bromo-3-methylbutane. Assuming that the intermediate cut between these two compounds consisted of equal amounts of both isomers, 2-bromo-3-methylbutane represents 22% of the remaining amyl bromides. It was confirmed in a separate careful distillation that mere distillation under our conditions will not isomerize *t*-amyl bromide.

Chloride from Methylcyclohexane.—*t*-Butyl chloride (48 g., 0.52 mole) dissolved in 100 g. of methylcyclohexane (1.02 moles) was shaken with 10 g. of aluminum chloride powder (0.075 mole) for one minute and then quenched with water, the organic layer washed with water and carbonate solution. During the reaction there was vigorous evolution of isobutane. Distillation of the dried solution through a modified Claisen flask yielded several fractions of which only the one (1-chloro-1-methylcyclohexane) boiling at 89–90° under 100 mm. pressure (or 68–70° under 40 mm.) was investigated. The yield of such material from this run combined with another identical one was 36 g. It had n^{23}D 1.4582.

By exhaustive hydrolysis and two steam distillations the corresponding alcohol (1-methylcyclohexanol) was obtained, b. p. (19 mm.) 60–65°, n^{21}D 1.4579. The phenylurethan, recrystallized from ligroin, melted at 104–105° (Mousseron and Granger[19] report 105°).

From the chloride, 5-(1-methylcyclohexyl)-2-furoic acid was prepared according to Reichstein,[20] who reports the melting point as 110°. Our sample showed a melting point of 112–113°.

Chlorination of Methylcyclohexane.—The purpose of this experiment was to ascertain whether the chlorine transfer using an alkyl halide and aluminum chloride led to results different from those obtainable by the direct chlorination of the hydrocarbon in the presence of aluminum chloride. Chlorine was bubbled into 50 g. (0.5 mole) of ice-cold methylcyclohexane until 12 g. (0.17 mole) was absorbed. Five grams of aluminum chloride was added, bringing about a vigorous reaction and a red color. After one-half minute the reaction was quenched with water and the product worked up as usual. The only portion of the product which could be 1-chloro-1-methylcyclohexane was the fraction at 85–88° under 100 mm. pressure. Of this there was only 0.98 g., n^{23}D 1.4617. The fractions were

Mm.	°C.	G.	
760	100–102	29.8	Methylcyclohexane
100	To 85	4.42	
	85–88	0.98	
24	To 58	.6	
	Bottoms	4.43	

It is clear that direct chlorination does not effect the clean conversion of the branched cycloparaffin into its chloro derivative which is achieved by the halogen–hydrogen exchange.

Chloride from Isopropylcyclohexane.—Treatment of 50 g. of isopropylcyclohexane with *t*-butyl chloride and aluminum chloride in the usual manner led to 14 g. of a chloride, b. p. (16–17 mm.) 85–86°, n^{23}D 1.4643, which could be hydrolyzed to an alcohol, b. p. (16 mm.) 78–83°, $n^{21.5}$D 1.4632. Although these correspond to the properties of 1-isopropylcyclohexanol,[21] we were not successful in preparing a crystalline phenylurethan or *p*-nitrobenzoate from it. Since a synthetic sample of the alcohol yielded these derivatives readily, we conclude that our chloride was far from pure. Isopropylcyclohexane has two tertiary hydrogen atoms and may be isomerized by aluminum chloride to cyclopentanes with two or three tertiary hydrogen atoms, so that a complex mixture of chlorides is not unexpected.

Chlorides from Decalin.—A solution of 17 g. of *t*-butyl chloride (0.185 mole) in 50 g. (0.362 mole) of decalin was shaken with 5 g. of powdered aluminum chloride for one-half minute before quenching with water. The products of two such runs were combined, washed, dried and distilled. No trace of *t*-butyl chloride remained. The first distillation, at 17 mm., yielded the cuts

°C.	G.
76-90	51.9
90-112	48.5
Residue	3 (black tar)

Redistillation of the second fraction under 4.5-5 mm. yielded 31.9 g. of liquid boiling at 90–91°, a 50.5% yield of chlorodecalin. This halide was converted by boiling with potassium hydroxide in absolute ethanol into a mixture of $\Delta^{1,9}$-octalin and $\Delta^{9,10}$-octalin, but by potassium hydroxide in 95% ethanol into $\Delta^{9,10}$-octalin and an unidentified mixture of saturated products.

Reaction of the Chlorodecalin with Absolute Alcoholic Alkali.—Ten grams of the halide was heated under reflux with potassium hydroxide in absolute ethanol (50 cc.) for nine hours. A heavy precipitate of potassium chloride formed. Water was added, the product extracted into ether and isolated by distillation. The following fractions were obtained.

	°C.	G.
At 21 mm.	81–86	1.32
	86–88	2.3
	89–95	1.19
At 13 mm.	86–104	0.6

One cc. of the first fraction was converted into a nitrosochloride: a solution consisting of the olefin, 3 cc. of glacial acetic acid, and 2 cc. of isoamyl nitrite was cooled to −30° and then treated dropwise with 2 cc. of concentrated hydrochloric acid. The resulting blue precipitate, collected and washed with acetone, melted at 80–82°. On recrystallization from a rather large volume of acetone a white solid was obtained which, after four more recrystallizations, melted at 121°. (Hückel and Naab[22] report

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[19] Mousseron and Granger, *Compt. rend.*, **206**, 1486 (1938).

[20] Reichstein and Eberhardt, *Helv. Chim. Acta*, **18**, 721–724 (1935).

[21] Auwers and Ellinger, *Ann.*, **387**, 223 (1912).

[22] Hückel and Naab, *ibid.*, **502**, 136 (1933).

127° as the melting point of the nitrosochloride from $\Delta^{1,9}$-octalin.) The mother liquor on concentration deposited blue crystals which, after two recrystallizations from acetone, melted at 90.5–91.5° (reported for $\Delta^{9,10}$-octalin nitrosochloride, 92°[22,23]).

Reaction of the Chlorodecalin with Potassium Hydroxide in 95% Ethanol.—The chlorodecalin (24.14 g., 0.14 mole) was heated under reflux for forty-eight hours with 10 g. of potassium hydroxide dissolved in 60 cc. of 95% ethanol. The product was worked up and separated by distillation into two fractions giving negative halogen tests even on warming

	°C.	G.	$n^{22.5}\text{D}$
1	82–90	10.36	1.4939
2	101–109	9.03	....

The bulk of Fraction 1 boiled at 86° and the bulk of Fraction 2 at 104–105°. The nitrosochloride of the first fraction was blue and melted at 90–92° on one crystallization with no evidence of the much more insoluble white nitrosochloride.

Carbonation of the Grignard Reagent from the Chlorodecalin.—Ten grams of the chloride dissolved in 35 cc. of dry ether was converted into the Grignard reagent over a period of four hours. The Grignard reagent was carbonated with carbon dioxide gas, the product hydrolyzed and worked up, being purified through the sodium salt. The acid was obtained as a colorless oil which soon solidified in a yield of 2.92 g. Crystallized from ligroin the acid melted at 103.8–105.6°. There was no evidence of any isomer separable from this.

Anal. Calcd. for $C_{11}H_{18}O_2$: C, 72.48; H, 9.96. Found: C, 72.43; H, 9.92.

From these results it is likely that the chlorodecalin consists of at least two isomers, one of which yields $\Delta^{9,10}$-octalin when treated with alkali in ethanol and is therefore one of the two 9-chlorodecalins or a mixture of the two. This product is to be investigated further.

Identification of Isopentane from Halogen–Hydrogen Exchanges with *t*-Amyl Halides.—Exchange reactions using *t*-amyl chloride or bromide lent themselves especially well to identification of the hydrocarbon product of the exchange. A three-necked flask was cooled in ice and fitted with a separatory funnel, a spiral condenser, and a mercury-sealed Hershberg stirrer.[24] The evolved gases were passed, first through a water scrubber to absorb hydrogen chloride, and then through a trap chilled with a dry-ice–toluene mixture to retain any gases condensable at −78°. The alkyl halide was added from the separatory funnel to a rapidly stirred mixture of paraffin and aluminum halide. The reaction was quenched by the addition of a small amount of water; the layers were separated and the organic layer was dried with a minimal quantity of anhydrous potassium carbonate and distilled, all precautions being taken to reduce loss as far as possible.

In one experiment we used 104 g. (0.75 mole) of decalin, 80 g. (0.75 mole) of *t*-amyl chloride and 4 g. (0.03 mole) of aluminum chloride. The mixture was stirred for two minutes. No hydrogen chloride or gas condensable at −78° was evolved during the run. The distillation of 177 g. of organic products yielded components as follows

Quantity, g.		Identity	B. p., °C.	Mm.	n_D
12.5	(0.17 mole)	Isopentane	29		1.354
53	(0.50 mole)	*t*-Amyl chloride	85		1.404
5	(0.05 mole)	3-Chloro-2-methylbutane?	53–56	220	1.407
71	(0.51 mole)	Decalin (*cis* + *trans*)	56–64	9	1.471–1.484
32	(0.19 mole)	Chlorodecalins	90–91 83	9 5	1.495
1.8		Residue			
1.7		Losses			

The boiling point and the refractive index of the isopentane are sufficient for positive identification. The other hydrocarbon most nearly approaching its properties is 2-methylbutene-1, b. p. 31°, $n^{20}\text{D}$ 1.378.[25] The nearly 1:1 relation between the molar quantities of chlorodecalins and isopentane found (0.19:0.17) recurs in other cases: from methylcyclohexane, 0.32 mole of methylchlorocyclohexane and 0.41 mole of isopentane; from 3-methylpentane and *t*-amyl bromide, 0.24 mole of bromohexanes and 0.31 mole of isopentane.

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Summary

In the presence of aluminum bromide halogen–hydrogen exchanges take place between tertiary or secondary alkyl halides and isoparaffins. For example, *t*-butyl chloride, isopentane, and aluminum bromide are converted into isobutane, *t*-amyl bromide, and aluminum chloride in the shortest time in which mixing can be effected. This time is estimated to be of the order of 0.001 second. As the duration of contact is increased, the *t*-amyl bromide is partly isomerized into 2-bromo-3-methylbutane and numerous products appear typical of low-temperature catalytic paraffin alkylations.

Halogen–hydrogen exchanges have been realized using isobutane, isopentane, 2,3-dimethylbutane, 2,2,3-trimethylbutane, methyl- and isopropylcyclohexanes, and decalin. Aluminum chloride as well as the bromide is effective. Poorly characterized products were obtained with 2,2,4-trimethylpentane, hydrindane, cholestane, camphane and bicyclo[2,2,1]heptane.

A mechanism for the halogen–hydrogen exchange is proposed whereby a carbonium ion is depicted as removing H: from the tertiary position in an isoparaffin. The exchange is thus regarded as an intermolecular analog of a process for which there is evidence in intramolecular rearrangements.

The demonstrated existence of the halogen–hydrogen exchange makes it possible to propose a mechanism of paraffin alkylation consisting only of steps which involve well-known types of reaction, and utilizing principles of reaction mechanism already amply demonstrated, notably by the work of Whitmore and his co-workers. Such a mechanism is outlined and its possible application to alkylation is indicated.

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(23) Campbell, THIS JOURNAL, **63**, 2725 (1941).

(24) Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

(25) Egloff, "Physical Constants of Hydrocarbons," Reinhold Pub. Corp., New York, N. Y., 1939, p. 179.