

The conditions under which such a copolymer is possible are described.

4. A method of approximating the integral

of the differential copolymerization equation is described.

PASSAIC, NEW JERSEY

RECEIVED JUNE 13, 1945

[CONTRIBUTION FROM THE UNIVERSAL OIL PRODUCTS COMPANY, CHICAGO, ILL.]

The Mechanism of the Alkylation of Paraffins

BY LOUIS SCHMERLING

The catalytic alkylation of isoparaffins with olefins has been studied extensively ever since the reaction was discovered by Ipatieff and Pines¹ more than a decade ago. A number of mechanisms,² none of which is completely satisfactory, were proposed during the succeeding years in order to explain how the reaction occurs. A mechanism which appears to have none of the objectionable features of the previous ones and which seems to give a truer picture of what occurs during alkylation was described³ in a recent "Communication to the Editor" of this Journal. The present paper presents a more complete discussion of the reaction scheme there outlined.

Previous Mechanisms

The principal difficulty encountered in developing a paraffin alkylation mechanism is the formulation of a rational explanation for the structure of the products obtained. As may be seen from Table I, the products of the alkylation of isobutane with ethylene and propene, for example, are not those which may be obtained by simple

addition of an alkyl group and a hydrogen atom across the olefinic double bond. A brief discussion of how each of the earlier mechanisms accounted for the products obtained is given below.

Ipatieff and Grosse^{2a} postulated that the alkylation of an isoparaffin proceeds via the addition of the corresponding *t*-alkyl group and hydrogen to the olefin to yield a paraffin containing a quaternary carbon atom; this compound is not isolated but undergoes isomerization to yield the isomeric products which are actually obtained. Thus, the alkylation of isobutane with ethylene would yield 2,2-dimethylbutane as the unstable intermediate and 2,3-dimethylbutane as the final product. The chief objection to this mechanism is that neohexane is the predominant hexane in equilibrium mixtures of hexanes at temperatures up to 200° and even higher.⁴ Therefore, it would be expected that a substantial amount of 2,2-dimethylbutane would be present in the alkylation product. Another objection to this mechanism is that in many cases, especially with sulfuric acid as catalyst, isomerization of the "expected" product does not take place under the conditions of the alkylation.^{2c,d}

The mechanism offered by Birch and Dunstan^{2b} differs from that of Ipatieff and Grosse in that it proposes that the alkylation involves a primary rather than the tertiary carbon atom. Alkylation of isobutane with propene, for example, would occur by way of addition of isobutyl and hydrogen to the double bond to yield 2,4-dimethylpentane. Isomerization of part of this heptane would then produce 2,3-dimethylpentane which is also a major product of the reaction. Birch and Dunstan suggest that the isoparaffin is activated (*via* the formation of a complex with the catalyst) and dissociates into a negative alkyl ion (in this example, isobutyl) and a proton, the proton coming from a methyl group. The olefin is activated by addition of a proton to form a positive alkyl ion (in this example, isopropyl). Combination of the carbanion (isobutyl) and the carbonium ion (isopropyl) yields the paraffinic product (2,4-dimethylpentane). The objections to the mechanism of Birch and Dunstan are similar to those raised against the mechanism of Ipatieff and Grosse, *i. e.*, the postulated isomerization of the primary product is improbable.^{2c}

(4) F. D. Rossini, E. J. R. Prosen and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **27**, 529 (1941).

TABLE I

COMPOSITION OF THE PRODUCTS OF THE ALKYLATION OF ISOBUTANE WITH ETHYLENE AND PROPENE IN THE PRESENCE OF ALUMINUM CHLORIDE AND HYDROGEN CHLORIDE

Olefin	Major products	Principal minor products ^a
Ethylene ^b	2,3-Dimethylbutane	2-Methylpentane Octanes Ethane Isopentane
Propene ^c	2,3-Dimethylpentane 2,4-Dimethylpentane	Trimethylpentanes Propane Isopentane 2,3-Dimethylbutane

^a References given below and unpublished results from the Research Laboratories of the Universal Oil Products Company. ^b A. V. Grosse and V. N. Ipatieff, *J. Org. Chem.*, **8**, 438 (1943). ^c H. Pines, A. V. Grosse and V. N. Ipatieff, *THIS JOURNAL* **64**, 33 (1942).

(1) V. N. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Co., New York, N. Y., 1936, p. 673.

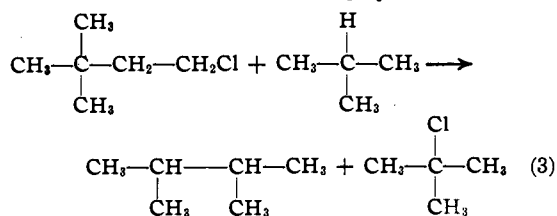
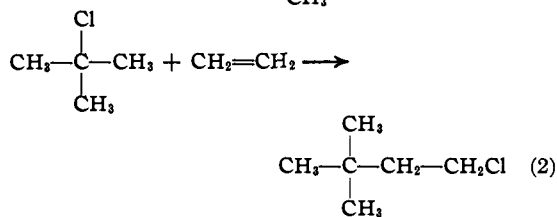
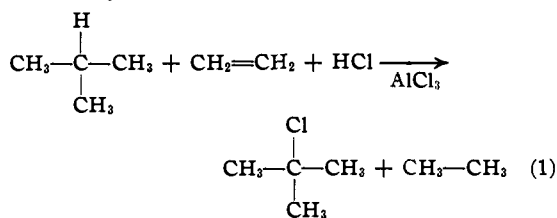
(2) (a) V. N. Ipatieff and A. V. Grosse, *THIS JOURNAL*, **57**, 1616 (1935); *J. Org. Chem.*, **8**, 438 (1943); Presented at Rochester Meeting of the American Chemical Society, September, 1937; (b) S. F. Birch and A. E. Dunstan, *Trans. Faraday Soc.*, **35**, 1013 (1939); (c) P. D. Caesar and A. W. Francis, *Ind. Eng. Chem.*, **33**, 1426 (1941); (d) S. H. McAllister, J. Anderson, S. A. Ballard and W. E. Ross, *J. Org. Chem.*, **6**, 647 (1941).

(3) L. Schmerling, *THIS JOURNAL*, **66**, 1422 (1944).

Caesar and Francis^{2c} and McAllister, Anderson, Ballard and Ross^{2d} proposed mechanisms which are similar in that each postulates that the isoparaffin undergoes carbon to carbon cleavage to yield two alkyl fragments (isopropyl and methyl, in the case of isobutane) which then add to the olefinic double bond to yield a paraffin. The mechanisms do account for the structures of the products obtained. However, in the case of the formation of 2,3-dimethylbutane by the alkylation of isobutane with ethylene, it is necessary to assume that the ethylene acts as if it were ethyldene. A similar postulation for the alkylation of isobutane with propene (*i. e.*, isopropylidene) would lead to the erroneous conclusion that triptane is formed in substantial amount. In short, these mechanisms appear to be rather artificial.

The Proposed Mechanism

The alkylation of isobutane with ethylene in the presence of aluminum chloride is used below in illustration of the mechanism. Similar reactions occur with other isoparaffins and olefins. The separate occurrence of each step in the mechanism has been proved rigidly only in the case of the aluminum chloride reaction. However, since the alkylation products obtained with other catalysts, including hydrogen fluoride and sulfuric acid, are similar to those obtained with aluminum chloride, it is presumed that analogous reactions occur with these other catalysts, the reaction intermediates being the *t*-alkyl fluorides and *t*-alkyl hydrogen sulfates, respectively, rather than the *t*-alkyl chlorides.



The *t*-butyl chloride formed in equation 3 starts a new cycle by reacting with ethylene as in equation 2. Ethane is produced only in the initiating step and the amount formed is, therefore, small.

"Casus Operandi."—As presented above, the mechanism shows the key steps which are believed to be involved in the alkylation of an isoparaffin with an olefin. It does not attempt to show how or why each step occurs. Thus, the addition of *t*-butyl chloride to the olefin may proceed by either a molecular or an ionic mechanism, either with or without the intermediate formation of an aluminum chloride complex, such as alkyl aluminum tetrachloride, RAlCl_4 . The hydrogen-chlorine exchange reactions (equations 1 and 3) may similarly involve molecules or ions and/or complexes. Present-day theory, of course, favors the ionic scheme; the rearrangement which occurs during the exchange reaction summarized by equation 3, is especially well explained by Whitmore's⁵ "common basis of intramolecular rearrangements" or the now so-called "carbonium ion" theory.⁶ However, in the present paper it seems desirable to emphasize the key steps of the reaction chain, to give experimental "molecular" proof of their feasibility, and to abstain insofar as possible from expressing the mechanism in terms of ions or other inner underlying motivators. It is quite probable that catalytic alkylation is motivated by the same forces that cause other catalytic reactions.

Subsequent to the publication of the above-discussed mechanism in condensed form,³ a partially similar mechanism was proposed by Ciapetta.⁷ The point of similarity is that Ciapetta assumes that a tertiary alkyl carbonium ion (or, in the molecular sense, ester) adds to the olefin to yield a carbonium ion of higher molecular weight which then undergoes carbon-skeleton rearrangement before being converted to the paraffin product. A very important point of difference is that Ciapetta does not use a chain mechanism for the continued conversion of the isoparaffin to the carbonium ion and of the olefin addition product to the final paraffin. Instead, he postulates that the isoparaffin loses a tertiary proton to yield a carbanion which then loses a pair of electrons to form the carbonium ion. In the final step, the proton and the electrons add to the carbonium ion of higher molecular weight, forming the paraffin product. The chain reaction scheme suggested by the present author appears to be preferable because it offers a more logical and plausible explanation for the conversion of the isoparaffin to the reactive tertiary alkyl chloride or carbonium ion; it is very highly improbable that free electrons can exist in a reaction mixture in the manner proposed by Ciapetta. Furthermore, if both carbanions and carbonium ions are formed, some of their interaction product (2,2,3,3-tetra-

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

(6) *Cf.* L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, chap. 10. For a discussion of the above-given alkylation mechanism in terms of carbonium ions, see ref. 11.

(7) F. G. Ciapetta, paper presented before the Petroleum Division of the American Chemical Society, New York City, September, 1944.

methylbutane in the case of isobutane) should be obtained. No evidence of the presence of this octane in an alkylation product has been found.

The Evidence

For Equation 1.—This probably occurs *via* the formation of ethyl chloride. Nenitzescu and Dragan⁸ found that an alkyl halide (*e. g.*, ethyl chloride) is reduced to the corresponding paraffin by reaction with another paraffin (*e. g.*, *n*-heptane) in the presence of aluminum chloride. The heptane is converted largely to higher boiling cycloparaffins as well as to the unsaturated hydrocarbons combined with the catalyst in the so-called "lower layer."

Similar results have been observed⁹ in a study of the reaction of isobutane with alkyl chlorides. The reaction of isobutane with isopropyl chloride at 40–70° gave from 60 to 90% of the theoretical yield of propane; the isobutane was converted chiefly to octanes and catalyst complex.

Ethane⁹ and propane^{2d, 9} have been obtained as by-products of the alkylation of isobutane with ethylene and propene, respectively.

That *t*-butyl chloride may be an intermediate in the reaction of isobutane with chlorohydrocarbons is shown by the fact that *t*-butyl chloride was isolated from the products of the reaction of isobutane with vinyl chloride¹⁰ and 2-chloropropene at temperatures near 0° or below.

Clear and striking confirmation of the first step of the mechanism may be found in the work of Bartlett, Condon and Schneider.¹¹ They showed that the *t*-alkyl halide derived from the isoparaffin may be isolated as such provided that short reaction times are used. For example, when a solution of aluminum bromide in isopentane is contacted with *t*-butyl chloride or isopropyl chloride at room temperature for as little as 0.001 sec., the principal product is *t*-amyl bromide, accompanied by a smaller amount of its isomerization product, 2-methyl-3-bromobutane. Isobutane and propane, respectively, were presumably also formed but were not isolated because of limitations of the apparatus used. On the other hand, isopentane was isolated from reactions involving *t*-amyl chloride or bromide.

It may be concluded that the conversion of an isoparaffin to an alkyl halide takes place rapidly under conditions such as obtain during alkylation.

For Equation 2.—An investigation of the condensation of alkyl halides with olefins in the presence of metal halide catalysts has shown that the primary reaction is that of addition of the alkyl group and the halogen atom to the double bond of the olefin. For example, a 75% yield of 1-chloro-3,3-dimethylbutane is obtained by the addition of *t*-butyl chloride to ethylene in the

presence of aluminum chloride at –15 to –10°. ¹² The reaction of *t*-butyl chloride with other olefins occurs in an analogous manner. The primary product of the reaction with propene, for example, is 2-chloro-4,4-dimethylpentane; under some conditions this is isomerized in part to 2- and 3-chloro-2,3-dimethylpentane.

For Equation 3.—The reaction involved in this step is essentially the same as that in equation 1, the chief difference being that in this case the isobutane reacts with an alkyl chloride of higher molecular weight. Excellent evidence that such chlorides are reduced to paraffins in the presence of isobutane may be found in the results obtained by the condensation of isobutane with allyl chloride in the presence of aluminum chloride.¹⁰ At low temperatures (below 0°) the chief product is 1-chloro-3,4-dimethylpentane. At higher temperatures interaction of this chloroheptane with excess isobutane results in the formation of heptane and other paraffinic hydrocarbons, the latter being produced by secondary reactions of the intermediate *t*-butyl chloride.

Direct proof that rearrangement of the carbon skeleton of the alkyl chloride occurs during its conversion to paraffin was obtained by showing that 2,3-dimethylbutane and *t*-butyl chloride are major products of the reaction of 1-chloro-3,3-dimethylbutane with isobutane in the presence of aluminum chloride at 22°; relatively little 2,2-dimethylbutane is formed. The rearrangement is not unexpected since a neopentyl system is involved.⁵ In some cases, as for example, in the formation of 2,3-dimethylbutane from ethylene or of 2,3-dimethylpentane from propene, the migration of the methyl group is preceded by the migration of one of the methylene hydrogens of the neopentyl group. In other cases, as for example in the formation of 2-methylpentane from ethylene or of 2,4-dimethylpentane from propene, the methyl group undergoes an α, γ -shift.

Inferential evidence that the hydrogen-chlorine exchange step occurs during alkylation may be obtained from the fact that dichloroalkanes are produced by the low-temperature condensation of isobutane with vinyl chloride and allyl chloride in the presence of aluminum chloride.¹⁰ These dichlorides are formed by the addition of *t*-butyl chloride to the chloroolefins in a manner similar to the reaction of equation 2. In the case of vinyl chloride, the resulting 1,1-dichloro-3,3-dimethylbutane undergoes the reaction analogous to equation 3 in only a very small amount; in other words, the condensation is largely "frozen" at the end of the second step, and the dichlorohexane is the chief product. In the case of allyl chloride, on the other hand, the 1,2-dichloro-4,4-dimethylpentane contains a secondary chlorine atom and the major portion reacts with isobutane to yield 1-chloro-3,4-dimethylpentane (the chief product) and *t*-butyl chloride. The isolation of the di-

(8) C. D. Nenitzescu and A. Dragan, *Ber.*, **66**, 1897 (1933).

(9) Unpublished results from these Laboratories.

(10) L. Schmerling, *This Journal*, **67**, 1438 (1945).

(11) P. D. Bartlett, S. E. Condon and A. Schneider, *ibid.*, **66**, 1531 (1944).

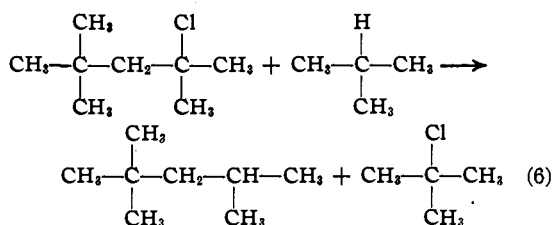
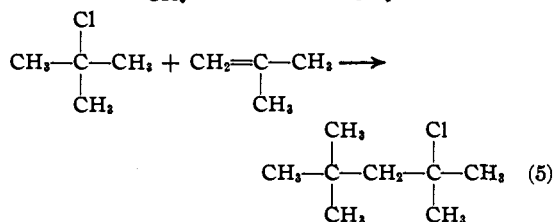
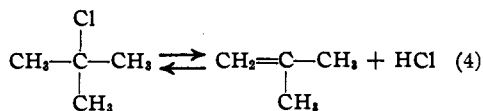
(12) L. Schmerling, *ibid.*, **67**, 1152 (1945).

chloroalkanes may be used as an argument in favor of employing a "molecular" rather than an ionic reaction scheme.

Alkylation of Normal Paraffins.—The present mechanism permits predictions with regard to the alkylation of normal paraffins. The exchange reaction of equation 1 (or of equation 3) does not take place as easily with hydrogen atoms attached to secondary carbon atoms as it does with those attached to tertiary carbon atoms.¹¹ Under the conditions required to obtain the hydrogen-halogen exchange reaction with normal paraffins, polymerization of the olefin (which may be considered to occur via a reaction similar to that of eq. 2) takes place very readily and becomes the predominant reaction. It may therefore be predicted that alkylation of *n*-paraffins will be relatively difficult.

Promoter Effect of Hydrogen Chloride.—The function of hydrogen chloride as promoter for the aluminum chloride catalyst in alkylation of isoparaffins presumably is to initiate and maintain the formation of the *t*-alkyl halide by the reaction of equation 1. Also, it may convert the metal halide to the more active acidic form, HAlCl_4 .

By-products.—Trimethylpentanes are products of all isobutane alkylations regardless of the olefin used. The formation of 2,2,4-trimethylpentane, for example, may be explained as follows

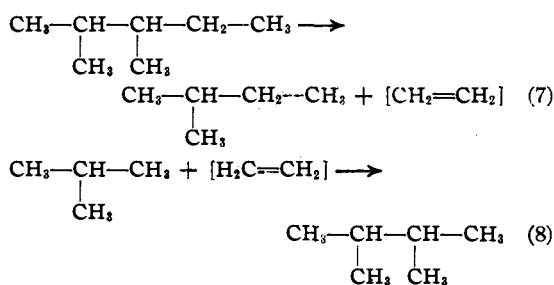


2,3,4-Trimethylpentane may be formed by rearrangement of the carbon skeleton during the last reaction. The octane by-product is probably identical with that obtained by alkylation of isobutane with isobutylene.

It will be noted that one molecule of *t*-butyl chloride is ultimately consumed for each molecule of trimethylpentane produced. Since the formation of this excess *t*-butyl chloride occurs by means of the reaction of equation 1 which involves the

reduction of the olefin to paraffin, it is obvious that the production of the trimethylpentane will be accompanied by the production of an equimolar quantity of a low-boiling paraffin corresponding to the olefin alkylating agent. Such has been found to be at least semiquantitatively the case.

The formation of paraffins containing a larger or smaller number of carbon atoms than the sum of those contained in the reacting isoparaffin and olefin is apparently due in part to further reaction of the primary products by dissociation into "new" paraffins and olefins and the subsequent reaction of these olefins (or their equivalents) with the original isoparaffin (as well as of the "new" paraffins with original olefin). Thus, in the alkylation of isobutane with propene, the formation of isopentane and 2,3-dimethylbutane may be indicated by equations 7 and 8.



Similarly, in the reaction of isobutane with ethylene, isopentane and heptane may be formed *via* dissociation of octane (formed as indicated in eqs. 4-6 or by alkylation of the 2,3-dimethylbutane with a second molecule of ethylene) into isopentane and propene or of hexane into pentane and methylene. Reactions of this type have been suggested¹⁸ to account for the products of the "autodestructive alkylation" of paraffins.

The dissociation may be considered to be either a dealkylation or a depolymerization reaction. It presumably involves the intermediate formation of chloroparaffins (or other esters or carbonium ions¹¹) by hydrogen-chlorine exchange followed by carbon-carbon cleavage.

Insight into another mode of formation of these by-products is furnished by the observation¹² that 1-chloro-3,3-dimethylpentane and 1-chloro-3,3-dimethylbutane are by-products of the condensation of ethylene with *t*-butyl chloride and *t*-amyl chloride, respectively. Partial conversion of either *t*-alkyl chloride into the other presumably occurs under the reaction conditions. It is apparent, then, that the alkyl chloride formed as indicated in equation 3 may be converted into a chloride of higher and/or lower molecular weight before undergoing the condensation step of equation 2 and that further reaction of the condensation product with isoparaffin yields the by-product paraffin and *t*-alkyl chloride in accordance with equation 3.

(13) V. N. Ipatieff and A. V. Grosse, *Ind. Eng. Chem.*, **26**, 461 (1934).

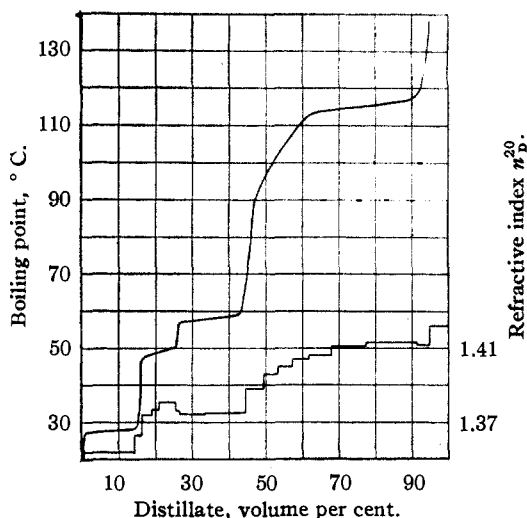


Fig. 1.—Distillation of product of the reaction of 1-chloro-3,3-dimethylbutane with butane.

Thermal Alkylation.—The alkylation of isobutane with ethylene at high temperatures and pressure in the absence of a catalyst yields 2,2-dimethylbutane (neohexane) and not 2,3-dimethylbutane.¹⁴ The difference may be explained by assuming that the thermal alkylation takes place by the direct addition of *t*-butyl and hydrogen (as free radicals rather than ions?) to the double bond of the olefin, producing a paraffin which does not isomerize under the reaction conditions and is isolated as such. In catalytic alkylation, as shown above, the primary product is an ester, the carbon skeleton of which rearranges during its conversion to paraffin.

Experimental

Direct evidence in support of equations 1 and 2 has already been published.^{11,12} The experimental data presented in the present paper will therefore be limited to proof that the reaction of equation 3 can occur.

Reaction of 1-Chloro-3,3-dimethylbutane with Isobutane.—Sixty-five grams (0.54 mole) of 1-chloro-3,3-dimethylbutane¹² (b. p. 41° at 50 mm. pressure; n_D^{20} 1.4160) and 130 g. (2.24 moles) of isobutane (Phillips Petroleum Company "Pure Product") were weighed into a glass tube (equipped with a ground-glass stopper containing a 1 mm. hole) which was cooled in a Dry Ice-acetone bath. Five grams of resublimed aluminum chloride (powder) was added, the tube was placed in an Ipatieff type autoclave, which was then sealed, and nitrogen was added up to a pressure of 30 atm. The autoclave was rotated at room temperature (22°) for two hours, after which the gaseous products were passed through a soda lime tower to absorb hydrogen chloride and into a trap immersed in a Dry Ice-bath. The autoclave was cooled to 0° before it was opened. The product in the liner consisted of a water-white liquid upper layer (containing dissolved butane) and a red-brown lower catalyst layer. The weights in grams of the various products were: material condensed at -78°, 53.0; liquid product, 126.5; catalyst layer, 10.5; hydrogen chloride, 9.0; and loss, 1.0.

The liquid product was decanted from the catalyst, combined with the product condensed at -78°. 3 g. of ice was added to decompose any trace of catalyst, and the

mixture was stabilized at 40°, leaving 64 g. of liquid. The gases were again passed through soda lime into a trap cooled by a Dry Ice-bath; 112 g. of condensate (92.6% butane and 3.8% C₃+, according to distillation through a Podbielniak column) were obtained. There was no further gain in weight of the soda lime.

Washing the stabilized liquid yielded only 0.1 g. more hydrogen chloride. The liquid was dried and then distilled through a Podbielniak column; the data which were obtained are plotted in Fig. 1. Analysis of the fractions boiling below 95° by means of their infrared absorption spectra¹⁵ gave the results which are summarized in Table I. The presence of chlorohexane in the higher boiling material made analysis by means of the infrared absorption spectra impractical. The composition of this material was therefore estimated from the refractive indices and densities of the various fractions.

The presence of *t*-butyl chloride was confirmed by chemical means by preparing the anilide derivative,¹⁶ m. p. 128°. The 2,3-dimethylbutane was characterized by its photobromination product,¹⁷ 2,3-dibromo-2,3-dimethylbutane, m. p. 168-169° (sealed tube):

TABLE II

COMPOSITION OF THE LIQUID PRODUCT OF THE REACTION OF 1-CHLORO-3,3-DIMETHYLBUTANE WITH ISOBUTANE

Product	Wt., g.	Moles	-% of theory ^a -	
			On charge	On reacted
Isopentane	11.6	0.161	30	46
<i>n</i> -Pentane	0.4	.005	1	1
2,2-Dimethylbutane	1.8	.021	4	6
<i>t</i> -Butyl chloride ^b	4.5	.049	9	14
2,3-Dimethylbutane	12.8	.178	33	41
Octanes ^c	12.0	.116
Chlorohexane	22.5	.187	35	..
Higher boiling	4.5

^a Based on the chlorohexane. ^b The infrared analysis showed that *s*- and isobutyl chlorides were not present in more than trace amounts, if at all. ^c The infrared absorption spectra of the fractions boiling above 95° were too complex (because of the presence of chlorohexane) to make quantitative analyses practical. The presence of 2,2,4-trimethylpentane was definitely indicated.

It will be noted that 0.54 minus 0.19, or 0.35 mole of 1-chloro-3,3-dimethylbutane reacted. There was obtained 0.18 mole of 2,3-dimethylbutane, 0.02 mole of 2,2-dimethylbutane and 0.17 mole of pentane or a total of 0.37 mole. The corresponding amount (0.35 mole) of *t*-butyl chloride was not isolated; 0.05 mole remained as such, the remainder reacting to form octanes (0.12 mole), higher boiling paraffins and catalyst layer complex. Under alkylation conditions (*i. e.*, when an olefin is added) the *t*-butyl chloride reacts with the olefin; under the conditions of the present experiment, the *t*-butyl chloride underwent the "polymerization" reaction illustrated by equation 4 to 6. Of the 0.35-gram atom of chlorine entering into the reaction, 0.25-gram atom was recovered as hydrogen chloride and 0.05-gram atom as *t*-butyl chloride, the remainder probably being present chiefly in the lower layer complex.

In the above calculations, it is assumed that the pentane was formed by the decomposition of the hexane. The weight balances seem to justify this assumption. On the other hand, at least part of the pentane was probably formed from the butane or octane (see above discussion on "By-Products"). The formation of 0.25 mole of hydrogen chloride would then be balanced by the forma-

(15) The writer is indebted to Dr. W. S. Gallaway of these Laboratories for the analyses.

(16) A. M. Schwartz and J. R. Johnson, *THIS JOURNAL*, **53**, 1063 (1931).

(17) V. N. Ipatieff and A. V. Grosse, *J. Org. Chem.*, **8**, 438 (1943).

(14) F. E. Frey and H. J. Hepp, *Ind. Eng. Chem.*, **28**, 1439 (1936).

tion of 0.12 mole of octanes plus part of the 0.17 mole of pentane plus some lower layer material.

A second experiment was carried out at a higher temperature. A glass liner containing 21 g. (0.17 mole) of 1-chloro-3,3-dimethylbutane, 77 g. (1.3 moles) of isobutane and 5 g. of aluminum chloride was placed in the autoclave, nitrogen was added to a pressure of 50 atm., and the autoclave was rotated at room temperature for one hour and then at 40° for three hours. The products consisted of 52 g. of isobutane, 20 g. of liquid product, 9 g. of a viscous red-brown catalyst layer and 4.5 g. of hydrogen chloride (73% of the theoretical yield) which was measured as the increase in weight of the soda lime tower in the exit line. The liquid product was completely paraffinic. No *t*-butyl chloride or unreacted 1-chloro-3,3-dimethylbutane was obtained. The reaction temperature was high enough to cause complete reaction of even the primary chloride. At least 90% of the liquid product boiled below 120°. Isopentane, 2,3-dimethylbutane and octanes were again the principal products of the reaction.

Summary

A chain mechanism which involves the following reactions is proposed for the alkylation of isoparaffins with olefins: 1. Conversion of the isoparaffin to a *t*-alkyl ester. 2. Addition of the *t*-alkyl ester to the olefin to yield an ester of higher molecular weight. 3. Reaction of the ester of higher molecular weight with the isoparaffin to yield the observed paraffin product and a new molecule of the *t*-alkyl ester.

The *t*-alkyl ester formed in the third step reacts with olefin as in the second step and the cycle is repeated.

Evidence in support of the mechanism is presented.

CHICAGO, ILL.

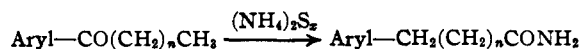
RECEIVED MARCH 8, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Willgerodt Reaction. I. The Use of Aliphatic Carbonyl Compounds¹

BY LIEBE CAVALIERI, DEXTER B. PATTISON² AND MARVIN CARMACK

Numerous examples of the use of the Willgerodt reaction with aryl alkyl ketones have appeared in the literature.^{3,4} Practically all of the successful reactions can be represented by the generalized equation



in which the aryl group may be any of a wide variety of aromatic nuclei not affected by the reagent, and *n* may vary from 0 to at least 4. The reaction is caused by the action of aqueous ammonium polysulfide on the ketone in a closed system at temperatures up to 200° or higher. The use of dioxane in addition to the ammonium polysulfide, introduced by Fieser and Kilmer,⁴ permits the Willgerodt reaction to be carried out at temperatures in the neighborhood of 160° and usually with better yields than in aqueous solution alone.

It appears to have been generally assumed that the presence of an aromatic group on the carbonyl unit is essential for the occurrence of the Willgerodt reaction, since there is no record of an attempt to apply the method to a completely aliphatic ketone. In an early paper, Willgerodt reported³ that acetone reacts with ammonium polysulfide

at room temperature to form a complex sulfur-containing compound of unknown structure, but he apparently did not study the reaction of acetone at the higher temperatures required for the formation of amides.

We have found that aliphatic carbonyl compounds of the type $\text{RCO}(\text{CH}_2)_n\text{H}$, in which R represents an aliphatic hydrocarbon radical, may undergo reactions with ammonium polysulfide reagent to yield products analogous to those from aryl alkyl ketones. The products have the structures represented by $\text{R}(\text{CH}_2)_n\text{CONH}_2$. This paper describes experiments with compounds in which *n* has values from 0 to 3. The carbon skeleton present in the starting compound remains unchanged in the final amide, a fact which is of considerable interest in connection with the formulation of a general mechanism for the Willgerodt reaction and the related Kindler reaction.^{5,6} Since, in the R group, the carbon atom directly attached to the carbonyl group may be primary, secondary, or tertiary, it can be seen that this extension of the Willgerodt reaction affords a new approach to the synthesis of branched chain as well as straight chain fatty acids and amides. Particular interest attaches to certain branched chain aliphatic acids because of their relationship to phthioic acid and the evidence that some, *e. g.*, β,β -dioctylbutyric acid, are bactericidal to tubercle bacilli.⁷

The equations shown below represent the reactions of a number of typical carbonyl compounds which we have studied. Yields of amides are indicated in parentheses.

(1) Material from this paper was presented before the Organic Division at the Spring Meeting held by the Philadelphia Section of the American Chemical Society in Philadelphia on June 13, 1945.

(2) A portion of a thesis submitted by Dexter B. Pattison to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

(3) Willgerodt, *Ber.*, **20**, 2467 (1887); **21**, 534 (1888).

(4) Fieser and Kilmer, *THIS JOURNAL*, **62**, 1354 (1940). A bibliography of earlier articles on the Willgerodt reaction appears as a footnote in this publication.

(5) Kindler and Li, *Ber.*, **74B**, 321 (1941).

(6) Schwenk and Bloch, *THIS JOURNAL*, **64**, 3051 (1942).

(7) Robinson, *J. Chem. Soc.*, 505 (1940).