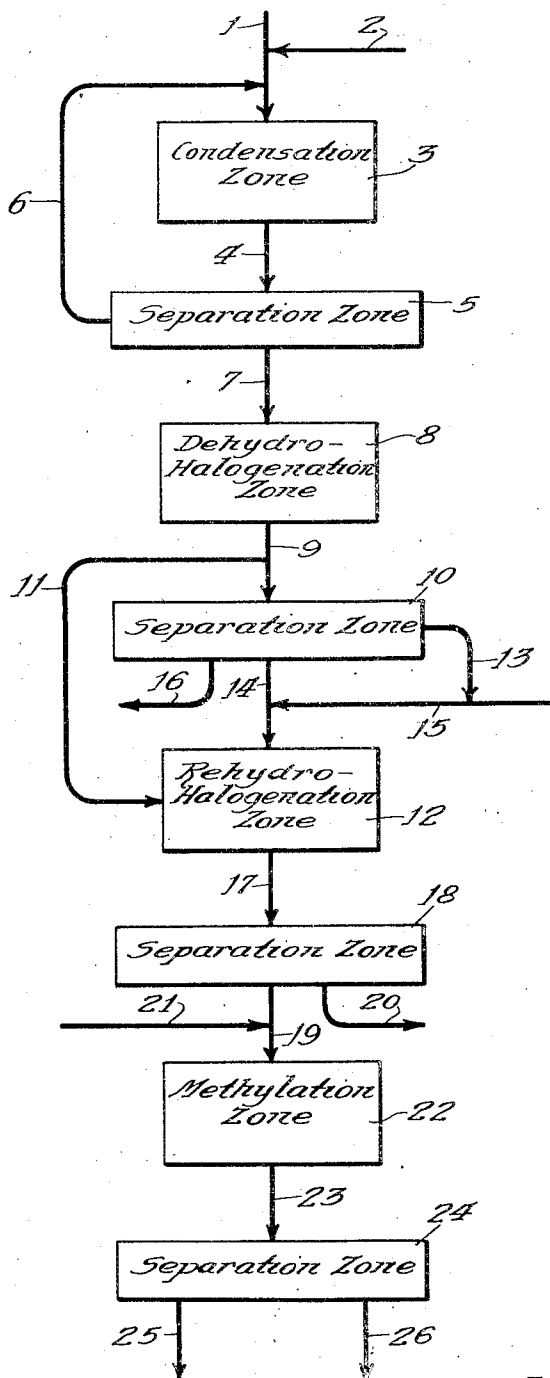


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MANUFACTURE OF ISOPARAFFINS

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MANUFACTURE OF ISOPARAFFINS

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This invention relates generally to processes for the production of paraffin hydrocarbons of branched chain structure. It is more specifically concerned with the manufacture of the isoparaffin hydrocarbon 2,2,3-trimethylbutane, commonly known as triptane.

The art of increasing the branching of paraffin hydrocarbons has been rapidly developing due to the fact that the more highly branched paraffins have been found to be more reactive chemically than the normal compounds and the more highly branched normally liquid paraffins have been found to possess high antiknock characteristics alone or in hydrocarbon blends used as fuel in internal combustion engines. The highly branched paraffin hydrocarbons have advantages over their olefinic counterparts in that they are more susceptible to increases in antiknock rating resulting from the addition of minor amounts of tetraethyl lead, and in their greater stability under storage conditions. The isoparaffins have advantages over aromatic hydrocarbons of comparable antiknock ratings in that they have much lower freezing points so that they have a greater safety factor when used in aviation fuel blends which are exposed to greatly reduced temperatures at considerable elevations above the earth's surface. The isoparaffins are better fuels than cycloparaffins on account of their generally higher antiknock value over cycloparaffinic compounds having equivalent boiling points.

A hydrocarbon which has been found to possess unusually high antiknock value both alone and in hydrocarbon motor fuel blends is the heptane, 2,2,3-trimethylbutane, which is the most highly branched heptane isomer. Antiknock rating of this hydrocarbon is abnormally high and its use in aviation engines has been found to increase the take-off load and the cruising speed of commercial and military airplanes and, therefore, the production of this hydrocarbon in commercial quantities would greatly enlarge the scope of usefulness of all types of airplanes. In its more particular aspect the present process can be applied to the manufacture of this particular hydrocarbon.

Numerous hydrocarbon reactions have been employed to produce highly branched paraffinic isomers. The normally or mildly branched paraffins have been isomerized in contact with various types of catalysts, particularly those of the Friedel-Crafts type and still more particularly the chloride and bromide of aluminum which are usually the most efficient of the compounds of

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the Friedel-Crafts group in isomerizing paraffin hydrocarbons. In such reactions better results are obtained in the presence of minor but critical amounts of added hydrogen halides and water. In these isomerization reactions, however, limits have been encountered in the degree of branching which can be obtained without suffering too great losses in the production of hydrocarbons due to concomitant decomposition reactions. Thus, as temperatures and times of catalytic contact are increased, there is a tendency for decomposition or cracking reactions to increase more rapidly than the true isomerization so that the overall production of more highly branched isomers is reduced along with the concurrent production of lower boiling paraffins and higher boiling residual compounds. In view of these difficulties, it has thus far been impossible to go beyond a certain degree of branching by the use of Friedel-Crafts catalysts. In the case of heptanes only small yields of triptane as representing the highest branched heptane have been produced although fairly good yields of dimethylpentanes have been obtained.

Another type of reaction which has been employed to produce isoparaffins of motor fuel boiling range has been the alkylation of isobutane, isopentane, etc. with olefin hydrocarbons in the presence of various catalysts including mineral acids and metal halides. Here, also limits have been found to the degree of branching in the alkylation products and alkylation reactions have not produced any substantial amounts of the 2,2,3-trimethylbutane.

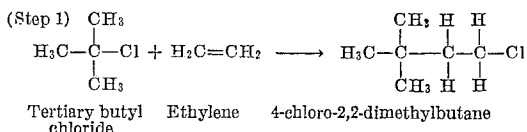
The present process involves a combination of interrelated steps whereby highly branched paraffin hydrocarbons such as triptane can be produced from low molecular weight olefins by a series of reactions.

In one specific embodiment the present invention comprises a process for the formation of highly branched iso-paraffin hydrocarbons which consists of the following steps: (1) reaction of a mono-olefin with an alkyl halide; (2) dehydrohalogenation of the alkyl halide produced in step 1; (3) rehydrohalogenation of the olefinic products from step 2; and (4) substitution of methyl groups for the chlorine atoms in the products from step 3.

While the steps of the process thus enumerated are generally applicable to tertiary alkyl halides and olefins of varying molecular weight and structure, as starting materials they are typified by the particular series of reactions which can be used for the manufacture of triptane.

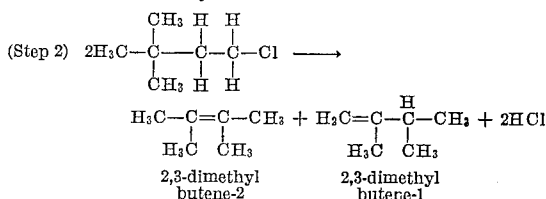
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The steps in the manufacture of this compound according to the present process are given in the equations and descriptive material which follows:



The above reaction may be conveniently brought about in the presence of such Friedel-Crafts type catalysts as ferric chloride, and bismuth chloride as representing the moderately active members of this group. To effect the above reaction in the presence of bismuth chloride, temperatures of from about 50 to about 125° C. are suitable and in the presence of such alternatively utilizable catalysts as ferric chloride or zirconium chloride, temperatures of from about -10 to about 50° C. are adequate. Reactions of the above character between tertiary alkyl halides and olefins may be further accelerated by the presence of small amounts of peroxides such as, for example, benzoyl peroxide, ascaridole, etc. Minor amounts of hydrogen halides also have a beneficial effect.

The second step of the process as applied to the manufacture of triptane involves the dehydrohalogenation of the primary hexyl chloride and the reaction involved is shown by the following equation in which the compounds are represented structurally:



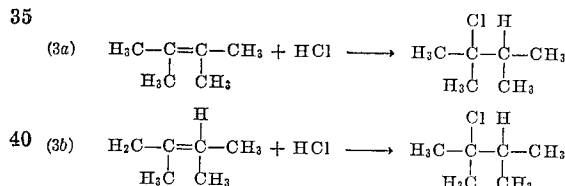
In the above equation it is indicated that equal molecular amounts of the two possible dimethylbutenes are produced from two molecules of the chloro compound. The production of exactly molecular proportions, however, does not take place but they will be formed in varying proportions depending upon the exact conditions of operation employed.

The dehydrohalogenation step may be brought about by contacting the alkyl halide with various alkaline reagents among which may be mentioned alkali metal hydroxides, alkaline earth metal oxides such as lime and magnesia and the commonly used commercial reagent known as soda lime. The dehydrohalogenation reactions may be brought about at varying temperatures depending upon the reagent employed for the reaction. Good yields of the olefins are obtainable with granular soda lime at temperatures of from about 300 to about 450° C. and the same range of temperature may be used if the alkali metal hydroxides or alkaline earth metal oxides are employed. When temperatures much lower than 200° C. are used, the reaction of dehydrohalogenation is slow and the rate is usually below that necessary for making the process practical. Another method of dehydrohalogenation for the production of olefins consists in heating the alkyl halides with water or aqueous solutions of acids, bases or salts at temperatures of from about 200 to about 250° C. and under relatively high pressures, due to the combined vapor pressure of the aqueous solution and the olefin. These pressures are commonly of the order of 200 to 250 pounds per square inch at a temperature of about 200° C.

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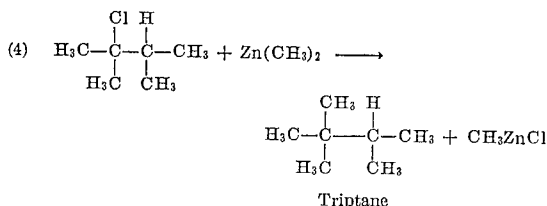
Still another method of dehydrohalogenation consists in contacting the alkyl halides with silica, clays or alumina, and particularly with alumina impregnated with alkaline earth metal halides, at temperatures of from about 200 to about 450° C. This method has the advantage that the products contain hydrogen halide in necessary amount for the next step of the process, namely the re-addition of hydrogen halide to the olefin. In such a case partial re-addition may occur spontaneously before the reaction product is recovered, and, the product from 4-chloro-2,2-dimethylbutane may consist of a mixture of hydrogen chloride, 2,3-dimethylbutenes and 2-chloro-2,3-dimethylbutane. Thus, the original primary chloride has in effect been isomerized to the desired tertiary alkyl chloride in one step.

It is to be noted that the olefin formed as a result of the dehydrohalogenation step correspond to a shift in the carbon atom structure, the methyl groups now appearing in the 2,3-position while they were in the 2,2-position in the alkyl halide. Therefore, in the next step of the process, involving the re-addition of hydrogen chloride, the chlorine appears in the 2-position, the hydrogen chloride having added according to Markownikoff's rule in which the halogen adds to a carbon atom and the hydrogen to (end carbon only in 2,3-dimethylbutene-1) the other carbon atom of the doubly bonded pair. The next step of the process, therefore, is represented by the following equation which shows the formation of the hexyl halide, 2,3-dimethyl-2-chloro-butane from either olefin:



In the above step hydrogen halide may be added at ordinary temperatures, practical reaction rates having been observed at temperatures of from about -80 to about +50° C. Metal halide catalysts are sometimes used. In the operation of the successive steps of dehydrohalogenation and rehydrohalogenation the desired change in structure of the chlorobutane may be brought about in successive zones in a reactor wherein the first zone contains granular dehydrohalogenating material such as alumina and is maintained at the optimum temperature for effecting the reaction and the second zone is cooled to a temperature corresponding to the re-addition of the hydrogen halide which was evolved in the first zone.

In the final step of the process the chlorine atom in the 2-position is replaced by a methyl group and in bringing about this substitution one of the more effective reagents is zinc dimethyl which reacts according to the following equation:



In conducting the above step a convenient method is to distill the zinc dimethyl into a sol-

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vent such as toluene or a paraffin hydrocarbon and then to slowly add a similar solution of the hexyl chloride at a temperature of the order of 5° C. which is below the temperature at which rapid reaction occurs. The solution is then warmed to a temperature within a range of from about 50 to about 90° C. and then refluxed for a period of about 2 hours, hydrolyzed by refluxing with water, the aqueous layer separated and the triptane distilled from the hydrocarbon solvent after which it may be given a light treatment with caustic soda to remove chlorine and other reaction products.

Alternatively with the use of zinc dimethyl for replacing chlorine with methyl groups in the final step of the process this reaction may be brought about by the use of methyl metal halides in dilute ether solutions according to the Grignard synthesis.

In such cases reactions between the alkyl chloride and the Grignard type reagents such as for example methyl magnesium chloride are brought about in relatively dilute ether solutions such as ethyl ether, and alternatively analogous compounds of aluminum, zinc or tin may be employed. Thus alternative methyl magnesium chloride may be formed by adding magnesium to an ether solution of methyl chloride and the reaction brought about by adding the hexyl chloride to the ether solution. As a further alternative the solution in ether of the 2-chloro-2,3-dimethyl butane may be treated with finely divided metallic magnesium until the compound 2,3-dimethyl butyl-2-magnesium chloride is formed and this compound is then reacted with methyl chloride or methyl sulfate preferably at room temperatures or slightly below room temperature.

After the final step of the process has been completed the products are fractionated to separate the desired triptane and the solvents which may have been employed are re-used and the magnesium recovered from the magnesium chloride by any desired series of steps.

The description of the process in the preceding paragraphs has been given in connection with the manufacture of triptane as one application, but the process is broadly applicable to the formation of highly branched isoparaffin hydrocarbons of higher molecular weight than triptane by using as starting materials alkyl halides of higher molecular weight than butyl halides and higher molecular weight homologs of ethylene. Furthermore, in the final step wherein the chlorine in the chloroalkane is substituted by alkyl groups, these groups may be of higher molecular weight than the methyl groups which are used for the formation of triptane. When different compounds of analogous constitution are used in the successive steps of the process there will necessarily be changes in the optimum conditions in each step, although the general procedures will be substantially the same as those described in connection with the manufacture of triptane.

According to this invention, our process for producing paraffinic hydrocarbons of highly branched chain structures is illustrated by the flow-sheet given in the attached diagrammatic drawing. For the sake of simplicity, the following description of this flow-sheet is given to illustrate the process for producing triptane although other highly branched paraffins may be produced also by the combination of cooperative steps utilized in our process.

Referring to the drawing, ethylene is introduced through line 1 in which this gaseous olefin is com-

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mingled with tertiary butyl chloride introduced through line 2. The mixture of ethylene and tertiary butyl chloride is then directed from line 1 to condensation zone 3 preferably containing a catalyst of the Friedel-Crafts type in order to condense tertiary butyl chloride and ethylene to form 4-chloro-2,2-dimethylbutane. As hereinbefore set forth, this condensation reaction is carried out at a temperature of from about 50° to about 125° C. in the presence of bismuth chloride, but different temperatures are generally employed when utilizing ferric chloride, aluminum chloride, aluminum bromide, etc. The reaction mixture from condensation zone 3 is conducted through line 4 to separation zone 5 in which unconverted ethylene and tertiary butyl chloride are separated from the higher boiling condensation product, hereinbefore referred to as 4-chloro-2,2-dimethylbutane. The unconverted ethylene and tertiary butyl chloride are recycled through line 6 and line 1 to condensation zone 3.

In the second step of the process as applied to the manufacture of triptane, the 4-chloro-2,2-dimethylbutane is directed from separation zone 5 through line 7 to dehydrohalogenation zone 8 preferably containing a dehydrohalogenation catalyst which promotes the splitting of hydrogen chloride from said 4-chloro-2,2-dimethylbutane and results in the formation of a mixture of 2,3-dimethylbutene-1 and 2,3-dimethylbutene-2. Dehydrohalogenation may also be carried out in the presence of various alkaline reagents but in these cases the hydrogen chloride combines chemically with the alkaline reagent and is not readily available for further use in the process. Such further use of hydrogen chloride may be made when a dehydrohalogenation catalyst is utilized.

The reaction mixture from dehydrohalogenation zone 8 is directed therefrom through line 9 and may be conducted to separation zone 10 or passed through line 11 to rehydrohalogenation zone 12. In the process for producing triptane, it is generally not necessary to utilize separation zone 10 as the entire reaction mixture produced in dehydrohalogenation zone 8 generally has the proper proportions of dimethylbutenes and hydrogen chloride needed for reaction in rehydrohalogenation zone 12 in which hydrogen chloride adds to the 2-position of each of the 2 isomeric 2,3-dimethylbutenes forming 2,3-dimethyl-2-chlorobutane.

Also if the dehydrohalogenation reaction is not complete in zone 8, the resultant mixture of hydrogen chloride, 2,3-dimethylbutene-1 and -2 and unconverted 4-chloro-2,2-dimethylbutane is directed to separation zone 10. Hydrogen chloride is conducted from separation zone 10 through lines 13 and 15 to line 14, the latter being also employed for conducting the mixture of 2,3-dimethylbutene-1 and -2 to rehydrohalogenation zone 12. If necessary, hydrogen chloride from an outside source may also be added through line 15. Unconverted 4-chloro-2,2-dimethylbutane which is separated from lower boiling materials in separation zone 10 may be withdrawn therefrom through line 16 and thence may be recycled to zone 8 by means not illustrated in the diagrammatic drawing.

The reaction mixture obtained in rehydrohalogenation zone 12 is directed through line 17 to separation zone 18 in which 2,3-dimethyl-2-chlorobutane is separated from any excess of hydrogen chloride, or from small amounts of by-products. The purified 2,3-dimethyl-2-chlorobutane is directed from separation zone 18 through

line 19 and the hydrogen chloride and/or by-products are withdrawn through line 20 to waste or storage not indicated in the diagrammatic drawing.

In the final step of the process, the 2,3-dimethyl-2-chlorobutane is commingled in line 19 with a methylating agent such as zinc dimethyl added thereto through line 21 and the resultant commingled mixture is then conducted to methylation zone 22 in which the chlorine atom of the 2,3-dimethyl-2-chlorobutane is replaced by a methyl group to form triptane. As hereinabove set forth, this replacement of a chlorine atom by a methyl group may also be carried out by utilizing a Grignard type reagent such as methyl magnesium chloride. The reaction mixture so formed in methylation zone 22 is withdrawn therefrom through line 23 to separation zone 24 in which triptane is separated from the reaction mixture. Triptane is withdrawn from separation zone 24 through line 25 to storage. The other constituents of the reaction mixture are discharged from separation zone 24 through line 26.

When the process of our invention is employed for producing a highly branched paraffin hydrocarbon other than triptane, suitable changes are made in the different steps of the process by employing an appropriate alkyl halide and a suitable olefin as starting materials. The essential feature of this process for producing highly branched chain paraffin hydrocarbons comprises the series of cooperative steps involving condensation of an alkyl halide and an olefin, dehydrohalogenation of the resultant condensation product, rehydrohalogenation of the olefins formed by the dehydrohalogenation step, and methylation of the higher molecular weight alkyl halide formed in the rehydrohalogenation step. Thus when producing some highly branched chain paraffin hydrocarbons, it is advisable to subject the dehydrohalogenation reaction mixture obtained in zone 3 to separation in separation zone 10 before conducting the desired olefinic hydrocarbons to rehydrohalogenation zone 12. In some cases, it may be necessary to discard some of the olefinic isomers from zone 10 through line 15 and to direct a chosen olefinic hydrocarbon through line 14 to rehydrohalogenation zone 12. In the above described process for producing triptane, the 2 olefins formed by the dehydrohalogenation reaction were of such structures that they yielded the same alkyl halide when rehydrohalogenated and thus the use of separation zone 10 was optional.

The following example is given to illustrate the character of results obtainable in the practical operation of the process, although it is not intended that the specific data given should unduly circumscribe the proper scope of the invention.

Tertiary butyl chloride is reacted with ethylene in the presence of bismuth chloride, the two compounds being contacted in approximately equimolecular proportions. The temperature employed is 60° C. and it is found that 4-chloro-2,2-dimethyl butane is produced in 75 per cent of the theoretical yield.

The 4-chloro-alkane is then vaporized and passed over granular alumina at a temperature of 325° C. and atmospheric pressure and the hydrogen halide and olefins produced are re-combined at atmospheric temperature to form the 2-chloro-2,3-dimethyl butane in 90 per cent theoretical yield. The isomerized hexyl chloride is separated by fractional distillation from the other reaction products.

To produce the desired triptane a solution of

the 2-chloro-2,3-dimethyl butane in toluene is slowly added to a toluene solution of zinc dimethyl at a temperature of 5° C. until there is a slight molar excess of methyl groups in relation to the chlorine atoms present in the hexyl chloride. The toluene solution of the two reactants is then maintained at a temperature of 80° C. for two hours under a reflux condenser, after which the solution is cooled and refluxed with an equal volume of water to effect hydrolysis and solution of the zinc salts.

The hydrocarbon layer from the aqueous treatment is then distilled to recover triptane which boils at 81° C. The overall weight yield of triptane based on the combined weight of the tertiary butyl chloride and ethylene originally reacted is 40 per cent.

We claim as our invention:

1. A process for the manufacture of isoparaffin hydrocarbons which comprises reacting an alkyl halide with a mono-olefin to produce a higher molecular weight alkyl halide, successively dehydrohalogenating said alkyl halide to produce an olefin, rehydrohalogenating said olefin to produce an isomer of said higher molecular weight alkyl halide and substituting a methyl group for the halogen atom in said last-named alkyl halide.

2. A process for the manufacture of isoparaffin hydrocarbons which comprises reacting a tertiary alkyl halide with a mono-olefin in the presence of a Friedel-Crafts type catalyst to produce a higher molecular weight alkyl halide, dehydrohalogenating said higher molecular weight alkyl halide in the presence of a catalyst to produce a mixture of olefins, reacting said olefins with a hydrogen halide to produce isomerized higher molecular weight alkyl halides, and substituting methyl groups for the halogen atoms in said alkyl halides.

3. A process for the manufacture of isoparaffin hydrocarbons which comprises reacting a tertiary alkyl halide with a mono-olefin in the presence of a Friedel-Crafts type catalyst at a temperature of from about -10° C. to about 125° C. to produce a higher molecular weight alkyl halide, dehydrohalogenating said higher molecular weight alkyl halide in the presence of a catalyst at a temperature of from about 200 to about 450° C. to produce a mixture of olefins, reacting said olefins with a hydrogen halide at a temperature of from about -50 to about +50° C. to produce isomerized higher molecular weight alkyl halides, and substituting methyl groups for the halogen atoms in said alkyl halides.

4. A process for the manufacture of isoparaffin hydrocarbons which comprises reacting a tertiary alkyl halide with a mono-olefin in the presence of a Friedel-Crafts type catalyst at a temperature of from about -10° C. to about 125° C. to produce a higher molecular weight alkyl halide, dehydrohalogenating said higher molecular weight alkyl halide in the presence of a catalyst at a temperature of from about 200 to about 450° C. to produce a mixture of olefins, reacting said olefins with a hydrogen halide at a temperature of from about -50 to about +50° C. to produce isomerized higher molecular weight alkyl halides, and substituting methyl groups for the halogen atoms in said alkyl halides by reaction with a methyl magnesium halide.

5. A process for the manufacture of isoparaffin hydrocarbons which comprises reacting a tertiary alkyl halide with a mono-olefin in the presence of a Friedel-Crafts type catalyst at a temperature of from about -10° C. to about 125° C. to produce

a higher molecular weight alkyl halide, dehydrohalogenating said higher molecular weight alkyl halide in the presence of a catalyst at a temperature of from about 200 to about 450° C. to produce a mixture of olefins, reacting said olefins with a hydrogen halide at a temperature of from about -50 to about +50° C. to produce isomerized higher molecular weight alkyl halides, and substituting methyl groups for the halogen atoms in said alkyl halides by reaction with zinc dimethyl.

6. A process for the manufacture of 2,2,3-trimethylbutane which comprises reacting tertiary butyl chloride with ethylene in the presence of bismuth chloride at a temperature of from about 50 to about 125° C. to produce 4-chloro-2,2-dimethyl butane, dehydrohalogenating said 4-chloro-2,2-dimethyl butane in the presence of a catalytic agent at a temperature of from about 200 to about 450° C. to produce an olefinic mixture comprising essentially 2,3-dimethylbutene-1 and 2,3-dimethylbutene-2, reacting said olefinic mixture with hydrogen chloride to produce 2-chloro-2,3-dimethylbutane and substituting methyl groups for the chlorine atoms in said 2-chloro-2,3-dimethylbutane.

7. A process for the manufacture of 2,2,3-trimethylbutane which comprises reacting tertiary butyl chloride with ethylene in the presence of ferric chloride at a temperature of from about -10 to about +50° C. to produce 4-chloro-2,2-dimethyl-butane, dehydrohalogenating said 4-chloro-2,2-dimethyl butane in the presence of a catalytic agent at a temperature of from about 200 to about 450° C. to produce an olefinic mixture comprising essentially 2,3-dimethylbutene-1 and 2,3-dimethylbutene-2, reacting said olefinic mixture with hydrogen chloride to produce 2-chloro-2,3-dimethylbutane and substituting methyl groups for the chlorine atoms in said 2-chloro-2,3-dimethylbutane.

8. A process for the manufacture of 2,2,3-trimethylbutane which comprises reacting tertiary butyl chloride with ethylene in the presence of bismuth chloride at a temperature of from about 50 to about 125° C. to produce 4-chloro-2,2-dimethylbutane, dehydrohalogenating said 4-chloro-2,2-dimethyl butane in the presence of a catalytic agent at a temperature of from about 200 to about 450° C. to produce an olefinic mixture comprising essentially 2,3-dimethylbutene-1 and 2,3-dimethylbutene-2, reacting said olefinic mixture with hydrogen chloride to produce 2-chloro-2,3-dimethylbutane and substituting methyl groups for the chlorine atoms in said 2-chloro-2,3-dimethylbutane by reaction with methyl magnesium chloride.

9. A process for the manufacture of 2,2,3-trimethylbutane which comprises reacting tertiary butyl chloride with ethylene in the presence of ferric chloride at a temperature of from about

-10 to about +50° C. to produce 4-chloro-2,2-dimethylbutane, dehydrohalogenating said 4-chloro-2,2-dimethylbutane in the presence of a catalytic agent at a temperature of from about 200 to about 450° C. to produce an olefinic mixture comprising essentially 2,3-dimethylbutene-1 and 2,3-dimethylbutene-2, reacting said olefin mixture with hydrogen chloride to produce 2-chloro-2,3-dimethylbutane and substituting methyl groups for the chlorine atoms in said 2-chloro-2,3-dimethylbutane by reaction with methyl magnesium chloride.

10. A process for the manufacture of 2,2,3-trimethylbutane which comprises reacting tertiary butyl chloride with ethylene in the presence of bismuth chloride at a temperature of from about 50 to about 125° C. to produce 4-chloro-2,2-dimethylbutane, dehydrohalogenating said 4-chloro-2,2-dimethylbutane in contact with a catalytic agent at a temperature of from about 200 to about 450° C. to produce an olefinic mixture comprising essentially 2,3-dimethylbutene-1 and 2,3-dimethylbutene-2, reacting said olefin mixture with hydrogen chloride to produce 2-chloro-2,3-dimethylbutane and substituting methyl groups for the chlorine atoms in said 2-chloro-2,3-dimethylbutane by reaction with zinc dimethyl.

11. A process for the manufacture of 2,2,3-trimethylbutane which comprises reacting tertiary butyl chloride with ethylene in the presence of ferric chloride at a temperature of from about -10 to about +50° C. to produce 4-chloro-2,2-dimethylbutane, dehydrohalogenating said 4-chloro-2,2-dimethylbutane in contact with an alkaline catalytic agent at a temperature of from about 200 to about 450° C. to produce an olefinic mixture comprising essentially 2,3-dimethylbutene-1 and 2,3-dimethylbutene-2, reacting said olefin mixture with hydrogen chloride to produce 2-chloro-2,3-dimethylbutane and substituting methyl groups for the chlorine atoms in said 2-chloro-2,3-dimethylbutane by reaction with zinc dimethyl.

12. A process for the manufacture of a 2-chloro-2,3-dimethyl alkane which comprises subjecting a 4-chloro-2,2-dimethyl alkane to contact with a dehydrohalogenating catalyst to produce olefins therefrom and subsequently reacting said olefins with hydrogen chloride.

13. A process for the manufacture of 2-chloro-2,3-dimethyl butane which comprises subjecting a 4-chloro-2,2-dimethyl butane to contact with a dehydrohalogenating catalyst to produce olefins therefrom and subsequently reacting said olefins with hydrogen chloride.

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