Sept. 25, 1945. H. H. VOGE 2,385,555

CYCLOHEXENE PRODUCTION

Filed May 2, 1944

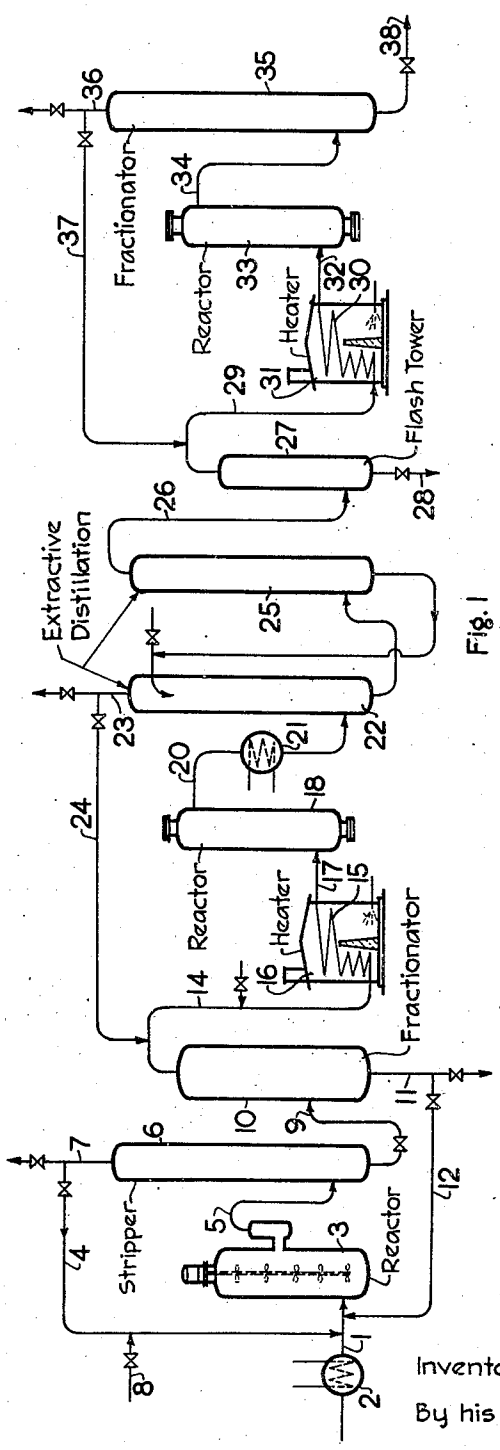


Fig. 1

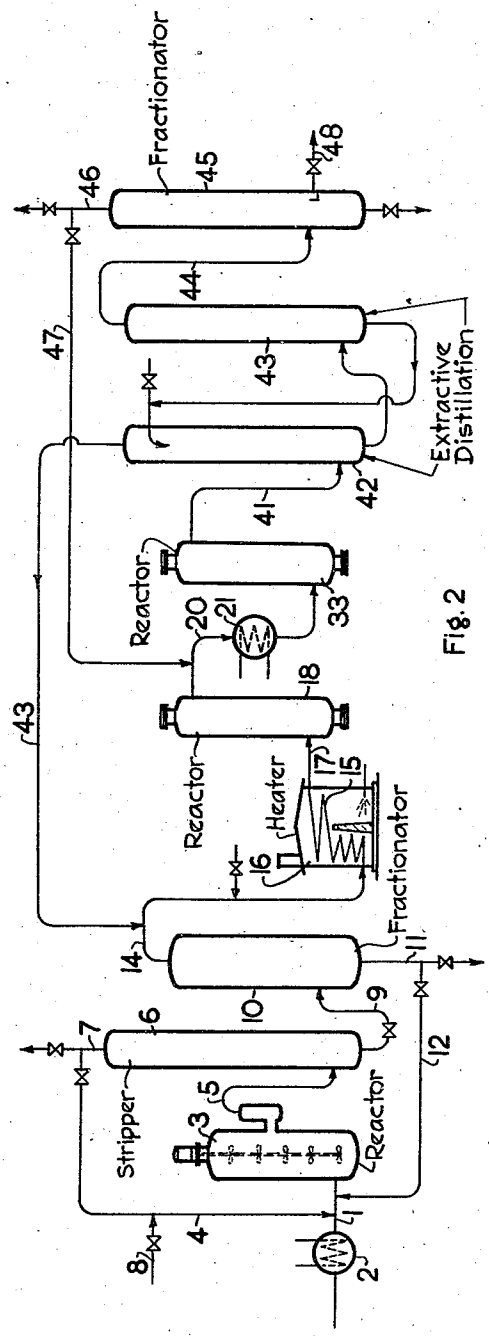


Fig. 2

Inventor: Hervey H. Voge

By his Attorney: C. J. Ott

Patented Sept. 25, 1945

2,385,555

UNITED STATES PATENT OFFICE

2,385,555

CYCLOHEXENE PRODUCTION

Hervey H. Voge, Berkeley, Calif., assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

Application May 2, 1944, Serial No. 533,763

11 Claims. (Cl. 260—666)

This invention relates to a process for the production of cyclohexene and relates more particularly to the conversion of cyclohexane to cyclohexene.

Of the unsaturated cyclic aliphatic hydrocarbons, cyclohexene finds application as the starting material for the production of a wide variety of valuable organic chemical derivatives which are themselves often important as intermediates in the manufacture of highly desirable products, such as for example, the polyamide resins. Heretofore, cyclohexene has generally been produced in a number of ways from more readily available materials by methods comprising the intermediate production of a compound from which the desired product could be produced with practical yields by available processes. Such intermediate compounds comprise, for example, a cyclohexyl halide, from which the desired cyclohexene is thereafter produced by such methods as high temperature treatments or by heating at lower temperatures with quinoline or alcoholic potash, by heating in the presence of water in the presence of alkaline agents etc. Such processes are not only often cumbersome, but are generally relatively costly because of the nature of the individual chemical processing steps involved. A process enabling the efficient manufacture of cyclohexene from a readily available material such as, for example, cyclohexane, in the absence of relatively complicated and costly intermediate chemical processing steps is, therefore, of the utmost importance. Production of cyclohexene on a practical scale by subjecting cyclohexane to heretofore disclosed dehydrogenation conditions is not feasible since the reaction cannot be controlled to result in economically attractive yields of the desired cyclic olefin and proceeds to the formation of a product consisting predominantly of benzene.

It is an object of the present invention to provide an improved process for the more efficient production of cyclohexene from cyclohexane or hydrocarbon mixtures comprising cyclohexane. Other objects and advantages of the invention will become apparent from the following description thereof.

In accordance with the process of the invention, cyclohexane, optionally in admixture with other hydrocarbons capable or not of undergoing conversion under conditions of execution of the process and/or in the presence of inert gaseous material, is contacted with an isomerization catalyst under naphthene isomerizing conditions effecting the conversion of cyclohexane to methylcyclopentane. Resulting methylcyclopentane is catalytically dehydrogenated to methylcyclopentenes, and the methylcyclopentenes thus obtained subjected to catalytic olefin isomerizing conditions effecting their conversion to cyclohexene.

Suitable charging material from which cyclohexene is produced in accordance with the invention comprises cyclohexane or cyclohexane-containing hydrocarbon mixtures obtained from any suitable source. Thus, the cyclohexane, or a hydrocarbon fraction comprising it, may be obtained by treatments comprising such steps as fractionation, solvent extraction, extractive distillation, etc., of naturally occurring hydrocarbon mixtures such as crude oils and natural gasoline, or of the products obtained in the thermal or catalytic treatment of such hydrocarbon mixtures or distillate fractions thereof. Such catalytic and thermal treatments comprise, for example, cracking, reforming, polymerization, destructive hydrogenation, etc.

In order to set forth more fully the nature of the invention, it will be described herein with reference to the attached drawing in which Figure 1 represents a more or less diagrammatic elevational view of one form of apparatus suitable for carrying out the process of the invention, and Figure 2 represents a more or less diagrammatic elevational view of one form of apparatus suitable for carrying out a preferred modification of the invention. Parts of apparatus of Figures 1 and 2, which are identical, are indicated with like reference characters.

Cyclohexane, or a hydrocarbon mixture comprising cyclohexane, is passed through line 1 and suitable heating means, for example, a furnace or heat exchanger 2, into a reaction zone. The reaction zone may comprise a reactor 3, for example of the mixer type. Within reactor 3, the hydrocarbon stream is contacted with an isomerization catalyst under naphthene isomerizing conditions. Suitable isomerization catalysts comprise those containing a metal halide of the Friedel-Crafts type, such as those comprising a halide of aluminum. Particularly suitable catalysts comprise aluminum chloride per se dissolved and/or suspended in the hydrocarbon charge; pre-formed fluid organo-aluminum halide complexes; isomerization catalyst of the molten salt type comprising, for example a molten mixture of an aluminum halide and one or more metal halides. A particularly advantageous catalyst of the molten salt type comprises a solution of aluminum chloride in molten antimony trichloride. The isomerization is carried out in

vapor or liquid phase. Particular operating conditions of temperature and pressure to be maintained within reactor 3 will vary in accordance with the type of catalyst used. Temperatures in the range of from about 50° C. to about 200° C. and preferably from about 70° C. to about 170° C. are suitable when utilizing isomerization catalysts comprising a metal halide of the Friedel-Crafts type. A hydrogen halide promoter, such as hydrogen chloride, in an amount ranging, for example, from about 0.1 to about 10% by weight of the charge, is introduced into line 1 by means of line 4. Higher or lower concentrations of the hydrogen halide promoter may be used. Under these conditions, cyclohexane is converted within reactor 3 to methylcyclopentane as exemplified by the following example.

Example I

A cyclohexane concentrate containing 83% by weight of cyclohexane and 15% by weight of open chain hexanes was contacted with a pre-formed aluminum chloride-hydrocarbon complex catalyst under the following conditions:

Temperature	140° C.
Time of contact	14 minutes
HCl promoter added	0.5% by weight of feed
Ratio of catalyst to hydrocarbon	1:1 by volume

A conversion of cyclohexane to methylcyclopentane of 40% was obtained.

From reactor 3, reactants are passed through line 5, into a stripping column 6 wherein a gaseous fraction comprising hydrogen chloride promoter is separated and recycled therefrom through valved lines 7 and 4 into line 1. Make-up hydrogen chloride is introduced into the system through valved line 8. Hydrocarbons comprising methylcyclopentane and unconverted cyclohexane, are passed from stripper 6, through valved line 9, into a fractionator 10. Hydrocarbons comprising unconverted cyclohexane are removed from fractionator 10 through valved line 11 and recycled at least in part through valved line 12 into line 1. Hydrocarbons comprising methylcyclopentane are removed overhead from fractionator 10 and are passed through line 14 into a heating zone, for example, an externally heated coil 15 positioned in a suitable furnace structure 16. From coil 15 the heated hydrocarbons are passed through line 17 into a reaction zone comprising, for example, a reactor 18.

Within reactor 18 the hydrocarbon stream is contacted with a suitable dehydrogenation catalyst, for example, one of the chrome-alumina type, such as a catalyst consisting essentially of an intimate mixture of oxides of chromium and aluminum, under dehydrogenation conditions effecting the conversion of methylcyclopentane to methylcyclopentenes. The temperature within reactor 18 is maintained in excess of about 500° C., for example, in the range of from about 450° C. to about 650° C. and preferably from about 500° C. to about 600° C. Temperature conditions are maintained by control of the heat input into the hydrocarbon stream flowing through heating coil 15. The dehydrogenation reaction is effected at atmospheric or superatmospheric pressure. Suitable pressures comprise pressures in the range of, for example, from about 1 to about 50 pounds absolute and preferably from about 10 to about 20 pounds absolute. Higher pressures may however be employed. Contact time in the range of from about 0.2 second to about 5 seconds have been found suitable with a liquid hourly space velocity of from about 0.5 to 10. Although a chromium oxide-aluminum oxide catalyst is chosen in the illustrative description of the invention as the dehydrogenation catalyst used in reactor 18, the invention is in no wise limited to the use of this particular catalyst. Other suitable dehydrogenation catalysts comprise, for example, oxides of metals of groups V and VI of the periodic table. These materials are preferably employed in combination with suitable dispersing bodying agents such as: oxides of metals of groups II, III and IV of the periodic table, particularly oxides of aluminum, magnesium, zirconium; bauxite; clays, such as the bentonites, montmorillonites, etc.; kieselguhr; crushed silica; glauconite sand; etc. Under these conditions, methylcyclopentane will be converted to methylcyclopentenes within reactor 18 as evidenced by the following example.

Example II

Methylcyclopentane was dehydrogenated by passage over a chromium oxide-alumina catalyst at 550° C. atmospheric pressure and a contact time of 1.1 seconds. A conversion of 26% was obtained. The converted material contained about 35% of methylcyclopentenes and 8% of conjugated diolefins.

From reactor 18, reaction products comprising gases, methylcyclopentenes, methylcyclopentadienes, higher boiling products, and unconverted methylcyclopentane are passed through line 20 and suitable cooling means, for example, indirect heat exchanger 21, to a suitable product separating zone wherein methylcyclopentenes are separated from hydrocarbons comprising methylcyclopentane by means which may comprise such steps as fractionation, solvent extraction, extractive distillation, etc. The product separating zone may comprise extractive distillation column 22. The extractive distillation is executed with the aid of a suitable solvent introduced into the upper part of column 22. Suitable solvents comprise, for example, phenols, cresylic acid, nitrobenzene, furfural, dichlorethyl ether, etc. Hydrocarbons consisting essentially of saturated hydrocarbons comprising methylcyclopentane are removed overhead from column 22 and recycled through valved lines 23 and 24 to line 14. Solvent comprising cyclic olefins is taken from column 22 and subjected to distillation within column 25. Solvent is returned from the lower part of column 25 to the upper part of column 22. Hydrocarbons comprising cyclic olefins are passed through line 26 into a flash tower 27. Within flash tower 27 any hydrocarbons higher boiling than methylcyclopentenes, are removed as bottoms while hydrocarbons comprising methylcyclopentenes are eliminated overhead and passed through line 28 to a heating zone. The heating zone may comprise an externally heated coil 30 positioned within a furnaced structure 31. The heated hydrocarbon stream is passed from coil 30 through line 32 into a reaction zone which may comprise an enlarged reaction chamber 33. If desired, materials higher boiling than C_6 hydrocarbons may be separated by suitable fractionating means not shown in the drawing before passage of the hydrocarbon stream from line 20 into the extractive distillation column 22. Conjugated diolefins may be separately recovered as valuable by-products by suitable means not shown comprising such steps as extraction, extractive distillation, compound formation, etc.

Within reactor 33 the methylcyclopentene stream is contacted, preferably in the vapor

phase, with a solid olefin isomerization catalyst, for example, a naturally occurring or synthetically prepared solid adsorptive aluminous material. Suitable olefin isomerization catalysts comprise, for example, aluminum oxides, Activated Alumina, bauxite, etc. These materials may be subjected to a pretreatment before use. Such pretreatments comprise, for example, subjection to elevated temperature, optionally in the presence of gaseous materials such as hydrogen, nitrogen, steam, gaseous materials comprising them, or contact with an inorganic mineral acid such as hydrogen chloride, etc. A particularly preferred type of catalyst comprises the adsorptive aluminous materials containing substantial amounts of gamma alumina that has been pretreated with an acidic material. By judicious control of heat input into coil 30, temperatures in the range of from about 300° C. to about 650° C., and preferably from about 350° C. to about 500° C., are maintained within reactor 33. Atmospheric or superatmospheric pressures may be maintained within reactor 33. Pressures close to atmospheric have been found suitable. A liquid hourly space velocity of, for example, from about 0.5 to about 25 is employed. Although adsorptive aluminous materials are preferred as catalysts for the isomerization of methylcyclopentenes, the invention is not necessarily limited thereto and other catalysts capable of activating the olefin isomerization reaction may be employed. Such catalysts comprise, for example, catalysts of the type of naturally occurring siliceous materials such as clays, bentonites or the like, alumina-silica compounds or mixtures thereof; zeolites; oxides of Be, Si, Ti, Th, V, Zr, Mn; etc. Other suitable catalysts are those comprising phosphoric acid and silica; as well as any acid of low volatility preferably on a solid oxide support material.

Under the above specified condition, methylcyclopentenes are converted to cyclohexene as evidenced by the following example.

Example III

Methylcyclopentenes were contacted with an HCl treated alumina at a temperature of 500° C. and atmospheric pressure at a liquid hourly space velocity of 19.2. Under these conditions about 12% of the charge was converted to cyclohexene and the balance consisted essentially of unreacted methylcyclopentenes. This represents a conversion of methylcyclopentenes to cyclohexenes equal to 80% of the equilibrium value for the temperature employed.

Reaction products comprising cyclohexene and unconverted methylcyclopentenes are passed through line 34 into a fractionator 35. Hydrocarbons comprising methylcyclopentenes are recycled from fractionator 35 through valved lines 36 and 37 into line 29. Hydrocarbons comprising cyclohexene are separated as a final product from fractionator 35 through valved line 38.

It has been found that methylcyclopentane when present in the methylcyclopentenes charged to reactor 33 will pass therethrough without any substantial part of the methylcyclopentane undergoing any change under the specified olefin isometrization conditions. In a modification of the invention as illustrated in Figure 2 of the drawing, effluence from the dehydrogenation reactor 18, comprising both methylcyclopentane and methylcyclopentenes, is passed through line 20 and cooling means 21, directly into isomerization reactor 33. In passing therethrough under the specified isomerizing conditions, the methylcyclopentenes are selectively converted to cyclohexene. Substantial saving in cost is thus obtained by utilizing the available heat content of the dehydrogenation reactor effluent in the subsequent isomerization reactor 33. Effluence from isomerization reactor 33 comprising methylcyclopentane, methylcyclopentenes, and cyclehexene is passed to an extractive distillation column 42 wherein it is extractively distilled in the presence of a suitable solvent capable of effecting separation of saturated hydrocarbons from cyclic olefins. Hydrocarbons comprising methylcyclopentane are taken overhead from column 42 and recycled through line 43 into line 14. Solvent comprising cyclic olefins is passed from column 42 into column 43 wherein separation of olefins and solvent is effected, the solvent being returned to the upper part of column 42. Hydrocarbons comprising methylcyclopentenes and cyclohexene are passed overhead from column 43 through line 44 into a fractionator 45. Hydrocarbons comprising methylcyclopentenes are separated as overhead in fractionator 45 and recycled through valved lines 46 and 47 to line 20 leading to the methylcyclopentene isomerization zone. The available heat content of the effluence from reactor 18 will generally suffice to raise the recycled methylcyclopentenes entering line 20 through line 47 to the desired isomerizing temperature. Additional adjustment of temperature within isomerizing reactor 33 is made by control of indirect heat exchanger 21. Hydrocarbons comprising cyclohexene are taken from fractionator 45 through valved line 48 as a final product.

For the purpose of clarity, all parts of apparatus not essential to a complete description of the invention comprising, for example, pumps, condensers, complete fractionating systems, accumulators, etc., have been omitted from the drawing. It is to be understood that the apparatus shown may be modified as apparent to one skilled in the art without departing from the scope of the invention.

I claim as my invention:

1. The process for the manufacture of cyclohexene from cyclohexane which comprises contacting cyclohexane with a catalyst comprising a metal halide of the Friedel-Crafts type under naphthene isomerizing conditions effecting the conversion of cyclohexane to methylcyclopentane, contacting the resulting methylcyclopentane with a dehydrogenating catalyst under dehydrogenating conditions effecting the conversion of methylcyclopentane to methylcyclopentenes, and contacting the resulting methylcyclopentenes with a solid olefin isomerizing catalyst under olefin isomerizing conditions effecting the conversion of methylcyclopentenes to cyclohexene.

2. The process for the manufacture of cyclohexene from cyclohexane which comprises contacting cyclohexane with a catalyst comprising a metal halide of the Friedel-Crafts type under naphthene isomerizing conditions effecting the conversion of cyclohexane to methylcyclopentane, contacting the resulting methylcyclopentane with a dehydrogenating catalyst under dehydrogenating conditions effecting the conversion of methylcyclopentane to methylcyclopentenes, and contacting the resulting methylcyclopentenes with a catalyst comprising a solid adsorptive aluminous material under olefin isomer-

izing conditions effecting the conversion of methylcyclopentenes to cyclohexene.

3. The process for the manufacture of cyclohexene from cyclohexane which comprises contacting cyclohexane with a catalyst comprising a halide of aluminum under naphthene isomerizing conditions effecting the conversion of cyclohexane to methylcyclopentane, contacting the resulting methylcyclopentane with a dehydrogenating catalyst under dehydrogenating conditions effecting the conversion of methylcyclopentane to methylcyclopentenes, and contacting the resulting methylcyclopentenes with a catalyst comprising adsorptive alumina under olefin isomerizing conditions effecting the conversion of methylcyclopentenes to cyclohexene.

4. The process for the manufacture of cyclohexene from cyclohexane which comprises contacting cyclohexane with a catalyst comprising aluminum chloride under naphthene isomerizing conditions effecting the conversion of cyclehexane to methylcylopentane, contacting the resulting methylcyclopentane with a dehydrogenating catalyst under dehydrogenating conditions effecting the conversion of methylcyclopentane to methylcyclopentenes, and contacting the resulting methylcyclopentenes with a catalyst comprising adsorptive alumina under olefin isomerizing conditions effecting the conversion of methylcyclopentenes to cyclohexene.

5. The process for the production of cyclohexene from hydrocarbons comprising cyclohexane which comprises contacting said hydrocarbons comprising cyclohexane with a catalyst comprising a metal halide of the Friedel-Crafts type under naphthene isomerizing conditions effecting the conversion of cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the isomerizate, contacting said hydrocarbons comprising methylcyclopentane with a dehydrogenating catalyst under dehydrogenating conditions effecting the conversion of methylcyclopentane to methylcyclopentenes, separating hydrocarbons comprising methylcyclopentenes from the products of said dehydrogenation, contacting said hydrocarbons comprising methylcyclopentenes with a solid olefin isomerizing catalyst under olefin isomerizing conditions effecting the conversion of methylcyclopentenes to cyclohexene, and separating hydrocarbons comprising cyclohexene from the products of said olefin isomerization.

6. The process for the production of cyclohexene from hydrocarbons comprising cyclohexane which comprises contacting said hydrocarbons comprising cyclohexane with a catalyst comprising a halide of aluminum under naphthene isomerizing conditions effecting the conversion of cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the isomerizate, contacting said hydrocarbons comprising methylcyclopentane with a dehydrogenating catalyst under dehydrogenating conditions effecting the conversion of methylcyclopentane to methylcyclopentenes, separating hydrocarbons comprising methylcyclopentenes from the products of said dehydrogenation, contacting said hydrocarbons comprising methylcyclopentenes with a catalyst comprising a solid adsorptive aluminous material under olefin isomerizing conditions effecting the conversion of methylcyclopentenes to cyclohexene, and separating hydrocarbons comprising cyclohexene from the products of said olefin isomerization.

7. The process for the production of cyclohexene from hydrocarbons comprising cyclohexane which comprises contacting said hydrocarbons comprising cyclohexane with a catalyst comprising a halide of aluminum under naphthene isomerizing conditions effecting the conversion of cyclohexane to methylcyclopentane, separating hydrocarbons comprising methylcyclopentane from the isomerizate, contacting said hydrocarbons comprising methylcyclopentane with a dehydrogenating catalyst under dehydrogenating conditions effecting the conversion of methylcyclopentane to methylcyclopentenes, separating hydrocarbons comprising methylcyclopentenes from the products of said dehydrogenation, contacting said hydrocarbons comprising methylcyclopentenes with a catalyst comprising adsorptive alumina under olefin isomerizing conditions effecting the conversion of methylcyclopentenes to cyclohexene, and separating hydrocarbons comprising cyclohexene from the products of said olefin isomerization.

8. The process for the production of cyclohexene from hydrocarbons comprising cyclohexane which comprises contacting said hydrocarbons comprising cyclohexane with a catalyst comprising a metal halide of the Friedel-Crafts type under naphthene isomerizing conditions effecting the conversion of cyclohexane to methylcyclopentane in a first conversion zone, separating hydrocarbons comprising methylcyclopentane from the effluence of said first conversion zone, contacting said hydrocarbons comprising methylcyclopentane with a dehydrogenating catalyst under dehydrogenating conditions effecting the conversion of methylcyclopentane to methylcyclopentenes in a second conversion zone, passing the effluence of said second conversion zone directly into a third conversion zone in intimate contact with a solid olefin isomerizing catalyst under olefin isomerizing conditions effecting the conversion of methylcyclopentenes to cyclohexene, and separating hydrocarbons comprising cyclohexene from the effluence of said third conversion zone.

9. The process for the production of cyclohexene from hydrocarbons comprising cyclohexane which comprises contacting said hydrocarbons comprising cyclohexane with a catalyst comprising a halide of aluminum under naphthene isomerizing conditions effecting the conversion of cyclohexane to methylcyclopentane in a first conversion zone, separating hydrocarbons comprising methylcyclopentane from the effluence of said first conversion zone, contacting said hydrocarbons comprising methylcyclopentane with a dehydrogenating catalyst under dehydrogenating conditions effecting the conversion of methylcyclopentane to methylcyclopentenes in a second conversion zone, passing the effluence of said second conversion zone directly into a third conversion zone in intimate contact with a catalyst comprising a solid adsorptive aluminous material under olefin isomerizing conditions effecting the conversion of methylcyclopentenes to cyclohexene, and separating hydrocarbons comprising cyclohexene from the effluence of said third conversion zone.

10. The process for the production of cyclohexene from hydrocarbons comprising cyclohexane which comprises contacting said hydrocarbons comprising cyclohexane with a catalyst comprising a halide of aluminum under naphthene isomerizing conditions effecting the conversion of cyclohexane to methylcyclopentane in

a first conversion zone, separating hydrocarbons comprising methylcyclopentane from the effluence of said first conversion zone, contacting said hydrocarbons comprising methylcyclopentane with a dehydrogenating catalyst under dehydrogenating conditions effecting the conversion of methylcyclopentane to methylcyclopentenes in a second conversion zone, passing the effluence of said second conversion zone directly into a third conversion zone in intimate contact with a catalyst comprising adsorptive alumina under olefin isomerizing conditions effecting the conversion of methylcyclopentenes to cyclohexene, and separating hydrocarbons comprising cyclohexene from the effluence of said third conversion zone.

11. The process for the production of cyclohexene from hydrocarbons comprising cyclohexane which comprises contacting said hydrocarbons comprising cyclohexane with a catalyst comprising a metal halide of the Friedel-Crafts type under naphthene isomerizing conditions effecting the conversion of cyclohexane to methylcyclopentane in a first conversion zone, separating hydrocarbons comprising methylcyclopentane from the effluence of said first conversion zone, contacting said hydrocarbons comprising methylcyclopentane with a dehydrogenating catalyst under dehydrogenating conditions effecting the conversion of methylcyclopentane to methylcyclopentenes in a second conversion zone, passing the effluence of said second conversion zone directly into a third conversion zone in intimate contact with a solid olefin isomerizing catalyst under olefin isomerizing conditions effecting the conversion of methylcyclopentenes to cyclohexene, separately recovering hydrocarbon fractions predominating in methylcyclopentane, methylcyclopentenes, and cyclohexene respectively, recycling said hydrocarbons comprising methylcyclopentane to said second conversion zone, and recycling said hydrocarbons comprising methylcyclopentenes to said third conversion zone.

HERVEY H. VOGE.