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METHYLCYCLOPENTENE PRODUCTION

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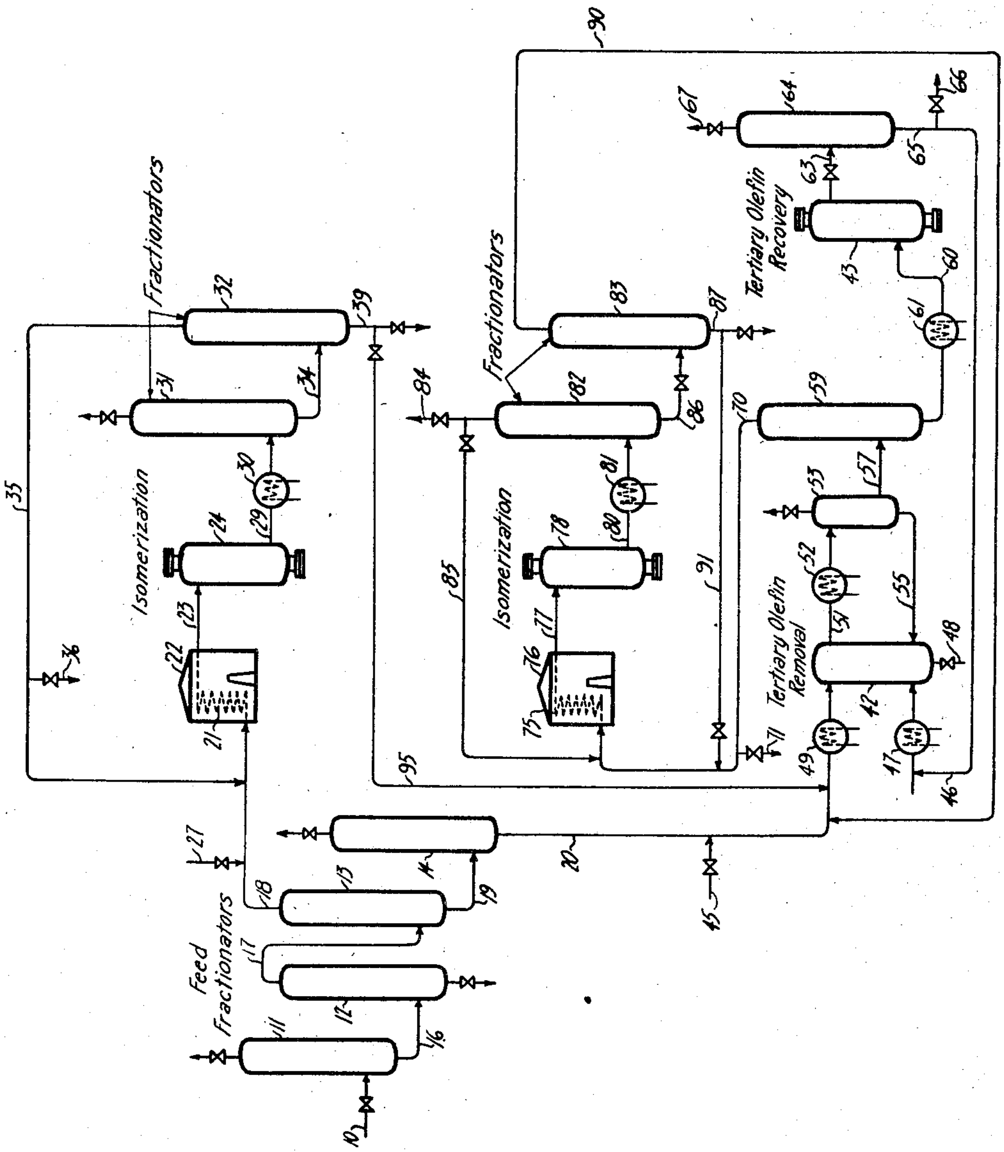

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METHYLCYCLOPENTENE PRODUCTION

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This invention relates to the production of cyclic olefins consisting essentially of methylcyclopentenes in a state of high purity. More particularly the invention relates to the production of cyclic olefins consisting essentially of methylcyclopentenes of high purity from complex hydrocarbon mixtures comprising methylcyclopentenes in admixture with close boiling hydrocarbons. A particular aspect of the invention relates to the production of cyclic tertiary olefins consisting essentially of 1-methylcyclopentene from hydrocarbon mixtures comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling hydrocarbons.

The methylcyclopentenes are valuable as intermediate and starting materials in the production of many valuable chemical derivatives. The need for these unsaturated cyclic compounds, in a state of relatively high purity, has rendered highly desirable suitable means enabling their more efficient production from readily available sources. Sources of the methylcyclopentenes comprise the olefinic hydrocarbon mixtures resulting from the thermal or catalytic treatment of naturally occurring or synthetically produced hydrocarbons or carbonaceous materials. The olefinic hydrocarbon mixtures boiling in the motor fuel boiling range obtained, for example, by the catalytic cracking of hydrocarbons, generally contain a substantial amount of methylcyclopentenes. The complexity of these hydrocarbon mixtures and the presence therein of a multiplicity of hydrocarbons boiling at temperatures in close proximity to the boiling temperatures of the methylcyclopentenes renders extremely difficult and often impossible the separation therefrom of these unsaturated cyclic hydrocarbons in a relatively high state of purity by methods available heretofore. The complexity of operative steps required, and in some cases the need for the use of catalysts or reagents of relatively high cost, to product methylcyclopentenes of a sufficient degree of purity by methods available heretofore, often render these processes highly impractical as a source of the desired unsaturated cyclic compounds. The difficulty of separating even a single one of the methylcyclopentene isomers from such hydrocarbon mixtures by methods available heretofore is rendered apparent by a realization of the multiplicity of hydrocarbons having approximating boiling temperatures generally present therein. Thus a hydrocarbon fraction consisting essentially of hydrocarbons having six carbon atoms to the molecule and having a boiling range of 65° to 69° C., separated from an olefinic cracked gasoline by fractionation will generally contain 3-methylcyclopentene in admixture with the closely boiling hydrocarbons indicated in the following table:

Table A

	°C.
2-ethylbutene-1	65
3-methylcyclopentene	67
2-methylpentene-2	67
3-methylpentene-2 (trans)	68
Hexene-3 (cis)	68
Hexene-3 (trans)	68
Hexene-2 (cis and trans)	68
n-Hexane	69

A fraction of such unsaturated cracked hydrocarbons boiling in the range of from 70° to 83° C. will generally contain 4-methylcyclopentene, 1-methylcyclopentene and methylenecyclopentane in admixture with the close boiling six carbon atom hydrocarbons indicated in the following table:

Table B

	°C.
3-methylpentene-2 (cis)	71
Methylcyclopentane	72
2,3-dimethylbutene-2	73
4-methylcyclopentene	75
1-methylcyclopentene	76
Methylenecyclopentane	76
Benzene	80
Cyclohexane	81
Cyclohexene	83

Close boiling hydrocarbons other than the six carbon atom hydrocarbons are generally encountered which further complicates the problem of separation as evidenced from the following table of seven carbon atom aliphatic hydrocarbons boiling in the range of from 72° to 85° C. encountered in olefinic cracked gasolines.

Table C

	°C.
4,4-dimethylpentene-1	72
4,4-dimethylpentene-2	76
3,3-dimethylpentene-1	77
2,3,3-trimethylbutene-1	78
2,2-dimethylpentane	79
2,4-dimethylpentane	81
2,4-dimethylpentene-1	81
3,4-dimethylpentene-1	81
2,2,3-trimethylbutane	81
2,4-dimethylpentene-2	82
3-methylhexene-1	84
2,3-dimethylpentene-1	85
3-ethylpentene-1	85
4-methylhexene-2 (trans)	85

The relatively wide spread in boiling range of the three methylcyclopentene isomers and the fact that the practicality of a process for the production of relatively pure methylcyclopentenes is often dependent upon a recovery of at least the greater part of all three, renders the use of processes involving such steps as fractionation and olefin extraction, as utilized heretofore, highly unsatisfactory.

It is an object of the present invention to provide an improved process for the more efficient production of cyclic olefins consisting essentially of methylcyclopentenes in a relatively high state of purity from olefinic hydrocarbon mixtures comprising methylcyclopentene in admixture with close boiling hydrocarbons inseparable therefrom on a practical scale by methods available heretofore.

Another object of the invention is the provision of an improved process for the more efficient production of cyclic olefins consisting essentially of methylcyclopentene of high purity from olefinic cracked hydrocarbon distillates.

Still another object of the invention is the provision of an improved process for the more efficient production of 3-methylcyclopentene of high purity from olefinic hydrocarbon fractions comprising 1-methylcyclopentene, and 4-methylcyclopentene in an admixture with close boiling open chain hydrocarbons.

A particular object of the invention is the provision of an improved process for the more efficient production of cyclic tertiary olefins of relatively high purity consisting essentially of 1-methylcyclopentene from olefinic hydrocarbon mixtures comprising methylcyclopentenes in admixture with close boiling hydrocarbons inseparable therefrom on a practical scale by methods available heretofore.

A more particular object of the invention is the provision of an improved process for the more efficient production of 1-methylcyclopentene of high purity from hydrocarbon fractions comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain hydrocarbons. Other objects and advantages of the invention will become apparent from the following detailed description thereof.

In co-pending application Serial No. 776,763 filed September 29, 1947, of which the present application is a continuation-in-part, there is disclosed and claimed a method for the production of methylcyclopentenes of high purity from hydrocarbon mixtures comprising methylcyclopentenes in admixture with close boiling open chain aliphatic hydrocarbons. In the method of the patent application the 1-methylcyclopentene is obtained, however, in admixture with substantial amounts of 4-methylcyclopentene, and the process does not lend itself to the efficient recovery of the methylcyclopentene content of the complex hydrocarbon charge in the form of only the 1-methylcyclopentene. Of the methylcyclopentene isomers, the 1-methylcyclopentene is of particular value because of the presence of a tertiary olefinic bond. Methylenecyclopentane, which at times may be present in smaller amounts, and which will be separated with the 1-methylcyclopentene according to the method of the present invention, is also a tertiary olefin and will generally give rise to chemical derivatives similar to or identical with those obtained from 1-methylcyclopentene in chemical processing.

In accordance with the process of the invention, methylcyclopentenes are produced from complex olefinic hydrocarbon mixtures comprising methylcyclopentenes in admixture with close boiling aliphatic hydrocarbons, with recovery of at least the greater part of said methylcyclopentenes in a high state of purity, by separating from said hydrocarbon mixture a hydrocarbon fraction comprising 3-methylcyclopentene and a hydrocarbon fraction comprising 1-methylcyclopentene and 4-methylcyclopentene and separately treating said fractions under the conditions defined fully herein to recover at least a substantial part of the methylcyclopentene content therefrom. In a preferred method of carrying out the process of the invention at least a substantial part of the methylcyclopentene content of the complex hydrocarbon charge is recovered as 1-methylcyclopentene of high purity.

The objects and advantages of the invention are obtained by fractionating a complex olefinic hydrocarbon mixture comprising methylcyclopentenes in admixture with close boiling aliphatic hydrocarbons from any suitable source, such as, for example, a catalytically cracked gasoline, to separate therefrom a lower boiling hydrocarbon fraction comprising 3-methylcyclopentene in admixture with close boiling aliphatic hydrocarbons having six carbon atoms to the molecule, and a higher boiling hydrocarbon fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling aliphatic hydrocarbons having seven carbon atoms to the molecule. The lower boiling hydrocarbon fraction is subjected to olefin isomerizing conditions in a first isomerizing zone effecting the conversion of 3-methylcyclopentene to cyclic olefins comprising 1-methylcyclopentene and 4-methylcyclopentene. The higher boiling fraction is subjected to tertiary olefin separating conditions, such as, for example, contact with an agent selectively combining with, or absorbing, the 1-methylcyclopentene in a tertiary olefin separating zone. Hydrocarbons comprising 4-methylcyclopentene in admixture with close boiling open chain hydrocarbons are separated from the effluence of the tertiary olefin separating zone and separately subjected to olefin isomerizing conditions in a second olefin isomerizing zone effecting the conversion of 4-methylcyclopentene to cyclic olefins comprising 1-methylcyclopentene. Effluence from the second isomerizing zone is returned to the tertiary olefin removing zone to effect the removal of 1-methylcyclopentene therefrom. 1-methylcyclopentene in a high state of purity is separated from the effluence of the tertiary olefin separating zone.

Optionally 3-methylcyclopentene in a high state of purity may be fractionated from the effluence of the second isomerizing zone and eliminated from the system as a final product. The process of the invention thus provides a highly flexible and efficient method for not only converting substantially the entire methylcyclopentene content of the complex hydrocarbon charge to methylcyclopentenes in a high state of purity but for the conversion of a substantial part of the methylcyclopentene content of the charge to 1-methylcyclopentene of high purity.

In a preferred modification of the invention substantially all of the methylcyclopentene content of the complex hydrocarbon charge is converted to essentially only 1-methylcyclopentene of high purity. In such preferred modification of the invention the 3-methylcyclopentene separated from the effluence of the second olefin isomerizing zone is recycled to the second olefin isomerizing zone to be converted to methylcyclopentenes comprising 1-methylcyclopentene therein. The 1- and 4-methylcyclopentenes emanating from the first as well as the second isomerizing zones are introduced into the tertiary olefin separating zone.

The process of the invention is applied to the separation of methylcyclopentenes in a high state of purity from complex hydrocarbon mixtures comprising them in admixture with close boiling aliphatic hydrocarbons obtained from any suitable source. Thus the charge to the system may comprise the methylcyclopentene-containing hydrocarbon mixtures obtained in the thermal or catalytic treatment of hydrocarbons, such as, for example, the methylcyclopentene-containing hydrocarbon mixtures obtained in the thermal and catalytic cracking, dehydrogenation, destructive dehydrogenation, reforming, and the like, of hydrocarbons.

In order to set forth more fully the nature of the invention, it will be described herein with reference to the attached drawing wherein the single figure represents a more or less diagrammatical elevational view of one form of apparatus suitable for executing the process of the invention.

Referring to the drawing, a complex olefinic hydrocarbon mixture comprising methylcyclopentenes in admixture with close boiling aliphatic hydrocarbons, such as, for example, a catalytically cracked gasoline, taken from an outside source is forced through valved line **10** into a feed fractionating zone. In the feed fractionating zone, the hydrocarbon charge is fractionated to separate therefrom a lower boiling fraction comprising 3-methylcyclopentene in admixture with close boiling aliphatic hydrocarbons and a higher boiling fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling aliphatic hydrocarbons. The feed fractionating zone is indicated in the drawing by fractionators **11**, **12**, **13** and **14**. Within fractionator **11** a vapor fraction comprising hydrocarbons boiling below about 66° C. is separated as a vapor fraction from a liquid fraction comprising hydrocarbons boiling above about 66° C. The liquid fraction is passed from fractionator **11** through line **16** into fractionator **12**. Within fractionator **12** a fraction comprising substantially all of the methylcyclopentene content of the charge, such as, for example, a fraction having a boiling range of from about 66° C to about 77° C., is separated as a vapor fraction from a liquidfraction comprising hydrocarbons higher boiling than about 77° C. The vapor fraction comprising isomeric methylcyclopentenes in admixture with close boiling aliphatic hydrocarbons is passed from fractionator **12** by means of line **17** into fractionator **13**. Within fractionator **13** a vapor fraction comprising 3-methylcyclopentene in admixture with close boiling hydrocarbons, such as, for example, a fraction boiling in the range of from about 66° C. to about 68° C. is separated as a vapor fraction from a liquid fraction comprising hydrocarbons boiling in the range of about 68° C. to about 77° C. The vapor fraction comprising 3-methylcyclopentene is taken overhead from fractionator **13** through line **18** and forms the charge to a first reaction zone.

The liquid fraction is passed from fractionator **13** through line **19** into fractionator **14**. Within fractionator **14** a vapor fraction comprising methylcyclopentane, such as, for example, a fraction boiling in the range of from about 68° C. to 74° C., is separated from a liquid reaction comprising substantially all of the 1-methylcyclopentene and 4-methylcyclopentene originally present in the charge in admixture with close boiling aliphatic hydrocarbons, such as, for example, a fraction boiling in the range of from about 74° C. to about 77° C. The liquid fraction comprising 1-methylcyclopentene and 4-methylcyclopentene is taken from fractionator **14** by means of line **20** and forms the charge to a separate reaction zone of the process.

The 3-methylcyclopentene-containing fraction flowing through line **18** will comprise a plurality of open chain olefinic hydrocarbons having six carbon atoms to the molecule boiling at, or close to, the boiling temperature of 3-methylcyclopentene and therefor inseparable therefrom on a practical scale by such expedients as fractionation.

The methylcyclopentene-containing fraction is passed from line **18** into a heating zone, such as, for example, an externally heated coil **21** positioned in a furnace structure **22**. From heating coil **21**, the heated 3-methylcyclopentene fraction is passed through line **23** into a suitable first reaction zone. The first reaction zone may comprise a reaction chamber **24**.

A hydrocarbon fraction consisting essentially of 3-methylcyclopentene in admixture with close-boiling aliphatic hydrocarbons may be introduced into line **18** from an outside source by means of valved line **27**. Such hydrocarbon fraction introduced into the system by means of line **27** may comprise a part or all of the 3-methylcyclopentene fraction introduced into the first reaction zone.

Within reaction chamber **24**, the 3-methylcyclopentene fraction is contacted with an olefin isomerization catalyst at olefin isomerizing conditions set forth fully below, effecting the conversion of 3-methylcyclopentene to unsaturated cyclic olefins consisting essentially of 1-methylcyclopentene, 4-methylcyclopentene and a minor amount of cyclohexene. Under the isomerizing conditions maintained in reactor **24** at least a substantial part of the six carbon atom open chain olefins are simultaneously converted to isomeric open chain olefins boiling below 66° C. Isomerization of the 3-methylcyclopentene fraction under these conditions is illustrated by the following example:

Example I

An olefinic hydrocarbon fraction having a boiling range of from about 66° C. to about 68° C., separated from a catalytically cracked gasoline by fractionation, and having a 3-methylcyclopentene content of 40% and an open chain C_6 olefin content of 55% is contacted with a bauxite catalyst at a temperature of 275° C. and atmospheric pressure. A conversion of 3-methylcyclopentene to 1-methylcyclopentene and 4-methylcyclopentene of 70%, and of open chain olefins to olefins boiling below 66° C. of 30% is obtained. Only about ½% of the 3-methylcyclopentene is converted to cyclohexene.

Effluence from reactor **24** comprising 1-methylcyclopentene, 4-methylcyclopentene, unconverted 3-methylcyclopentene, traces of cyclohexene, and the open chain isomerized and unisomerized six carbon atom olefins is passed through line **29**, provided with suitable cooling means, such as, for example, a heat exchanger **30**, into a product separating zone. Since the highest boiling noncyclic C_6 olefin boils at 73° C., and 1-methylcyclopentene, 4-methylcyclopentene, and cyclohexene boil at 75°, 76°, and 83° C., respectively, the 1- and 4-methylcyclopentenes along with the cyclohexene are readily separated from the reactor effluence by fractionation.

The product separating zone receiving reaction products from line **29** is depicted in the drawing by fractionators **31** and **32**. Within fractionator **31** a vapor fraction comprising isomerized open chain olefins boiling below 66° C. is separated from a liquid fraction comprising hydrocarbons boiling above 66° C. The liquid fraction is passed from fractionator **31** through line **34** into a fractionator **32**. Within fractionator **32** hydrocarbons comprising 1-methylcyclopentene, 4-methylcyclopentene as well as traces of cyclohexene are separated as a liquid fraction from a vapor fraction having a boiling range of about 66° to about 74° C. comprising unconverted 3-methylcyclopentene in admixture with close boiling aliphatic olefins. At least a part of the vapor fraction is recycled from fractionator **32**, through line **35**, into line **18**. Valved line **36** is provided to enable the bleeding of a portion of the recycle stream from the system to avoid the accumulation of saturated hydrocarbons boiling in the boiling range of the recycled stream. Although such bleeding will generally suffice, a portion or all of the recycle stream may be bypassed from line **35** through suitable saturated hydrocarbon removing means such as, for example, an extraction zone, not shown in the drawing.

The liquid fraction comprising 1- and 4-methylcyclopentenes, now free of any substantial amount of open chain hydrocarbons, is taken from fractionator **32** through valved line **39** and eliminated from the system as a final product. Any cyclohexene mixed with the methylcyclopentenes taken from valved line **39** is readily separable therefrom by fractionation.

The hydrocarbon fraction passing through line **20**, comprising 1-methylcyclopentene and 4-methylcyclopentene separated from the charge will comprise open chain heptenes having boiling temperatures closely approximating those of the methylcyclopentenes contained in the stream. These methylcyclopentene isomers are therefore inseparable from the open chain hydrocarbons admixed therewith, or from each other, by ordinary fractionating means. In accordance with the process of the invention the hydrocarbon stream flowing through line **20** is passed into a tertiary olefin separating zone.

Within the tertiary olefin separating zone the hydrocarbon stream is contacted with a treating agent such as a selectively reacting chemical agent capable of selectively reacting or combining with, or selectively absorbing, the cyclic tertiary olefin 1-methylcyclopentene. The tertiary olefin separating zone will generally comprise an olefin removing chamber wherein the tertiary cyclic olefin selectively reacts or combines with, or is selectively absorbed by, the tertiary olefin separating agent employed, and a tertiary olefin liberating chamber wherein the tertiary cyclic olefin (1-methylcyclopentene) is liberated from the reaction product, or rich absorbing medium, comprising it formed in the tertiary olefin removing zone. The tertiary olefin removing and liberating chambers may consist of separate sections comprised in a single vessel or may consist of separate vessels. In the drawing the tertiary olefin removing chamber and the tertiary olefin liberating chamber are represented by chambers **42** and **43**, respectively.

Additional hydrocarbons from an outside source consisting essentially of 1- and 4-methylcyclopentenes in admixture with close boiling open chain hydrocarbons having seven carbon atoms to the molecule may be introduced into the system by means of valved line **45**. Such hydrocarbons introduced into the system through valved line **45** may constitute a part or all of the hydrocarbons comprising 1- and 4-methylcyclopentenes in admixture with close boiling open chain hydrocarbons introduced into the system.

Within chamber **42** the hydrocarbon stream 1- and 4-methylcyclopentenes is contacted with a suitable treating or selectively reacting tertiary olefin separating agent, such as a chemical agent capable of entering into selective compound formation with the tertiary cyclic olefin, 1-methylcyclopentene, under compound-forming conditions. Thus the hydrocarbon stream may be contacted with a suitable alkylatable material under alkylating conditions within chamber **42**. Suitable alkylatable materials comprise, for example, the phenols such as the hydroxy aromatic compounds exemplified by phenol, cresol, resorcinol, hydroquinone, pyrogallol, naphthol, and the like. The alkylatable material, such as, for example, phenol, is introduced into chamber **42** from an outside source by means of valved line **46** provided with suitable heating means, such as, for example, a heat exchanger **47**. Within chamber **42** the phenol is intimately contacted with the hydrocarbons comprising 1- and 4-methylcyclopentenes in the presence of a suitable alkylating catalyst, such as, for example, sulfuric acid, phosphoric acid, aluminum chloride, stannic chloride, alkyl esters of sulfuric acid, and the like.

Conventional alkylating conditions effecting the selective alkylation of the phenol with the tertiary olefin, 1-methylcyclopentene, are maintained in chamber **42**. Temperatures ranging for example from about 0° C. to about 150° C. are maintained within chamber **42**. The specific temperature employed will, of course, vary in accordance with the particular catalyst employed. Thus temperatures in the range of, for example, from about 50° to 100° C. are suitable when employing a sulfuric acid catalyst. Temperatures in the range of, for example, from about 20° to about 85° C. are preferred when employing catalysts such as stannic chloride. With aluminum chloride catalysts lower temperatures, for example, from about 0° to about 50° C. are employed. Temperature conditions are maintained within chamber **42** by control of heat input into, or heat withdrawal from, the phenol stream by means of heat exchanger **47**, and the hydrocarbon stream by means of suitable heating means, such as an exchanger **49**, and optionally by additional temperature controlling means not shown in the drawing.

It is to be stressed that the process of the invention is in no wise limited to the use of any specific alkylating conditions within chamber **42** and conventional alkylating conditions enabling the alkylation of the alkylatable material with the 1-methylcyclopentene are maintained therein. Though phenols have been indicated as the preferred alkylatable material other alkylatable materials and corresponding alkylating conditions may be employed. Other suitable alkylatable materials comprise the hydroxy aromatic compounds having at least one replaceable nuclear hydrogen in the ortho or para position, such as chloro phenol, phenol sulfides, alkylphenolthioethers, etc.

Of the methylcyclopentenes, substantially only the 1-methylcyclopentene, in which the methyl side chain is directly linked to an unsaturated nuclear carbon atom, will react with the phenol under the alkylating conditions maintained within chamber **42**.

The manner of separation of the 1-methylcyclopentene from the 1-methylcyclopentene-containing fraction of the charge in accordance with the invention is illustrated by the following example:

Example II

A hydrocarbon fraction separated by fractionation from a catalytically cracked gasoline, boiling in the range of 74° to 77° C., having a 1- and 4-methylcyclopentene content of 70% is admixed with phenol and subjected to alkylating conditions at 85° C. in the presence of sulfuric acid. Alkylate is separated by fractionation and dealkylated by heating to 200° C. in the presence of concentrated sulfuric acid. Fractionation of the products of dealkylation results in the obtaining of 1-methylcyclopentene in an amount equal to about 90% of the 1-methylcyclopentene content of the gasoline fraction subjected to alkylation.

Effluence from chamber **42** comprising alkylated phenol, 4-methylcyclopentene, and open chain hydrocarbons is passed through line **51** provided with heat exchanger **52** into a separating chamber **53**. Within separating chamber **53** a hydrocarbon layer comprising alkylated phenol and 4-methylcyclopentene is separated from a catalyst layer. The catalyst is returned to chamber **42** by means of line **55** and the hydrocarbon layer is passed through line **57** into a fractionator **59**. Within fractionator **59** a vapor fraction comprising 4-methylcyclopentene and close boiling open chain hydrocarbons is separated from a liquid fraction comprising alkylated phenol.

The liquid fraction is passed from fractionator **59** through line **60** provided with suitable heating means, such as a heat exchanger **61**, into a chamber **43**. Optionally, the liquid fraction may be subjected to additional separating steps to effect the removal of at least a part of any reaction products other than the alkylated phenol therefrom prior to introduction into chamber **43**. Within chamber **43** the alkylated phenol is subjected to conditions effecting the liberation of the 1-methylcyclopentene from the 1-methylcyclopentene-phenol adduct formed in chamber **42**. Conditions employed to effect the liberation of the 1-methylcyclopentene may vary widely within the scope of the invention. Thus suitable dealkylating conditions to be maintained within chamber **43** comprise a temperature at least equal to the decomposition temperature of the alkylate assuring the splitting off of 1-methylcyclopentene from the phenol. Thus the temperature within chamber **43** may range from, for example, about 100° C. to about 450° C. The dealkylation may be effected in the presence of a suitable dealkylation catalyst, for example, a mineral acid, such as, phosphoric acid; acid treated clay, such as an acid treated silica-alumina; bauxite; zinc chloride; zinc chloride in combination with alumina; boric acid in combination with adsorptive alumina; etc. The specific temperature employed will vary in accordance with the specific type of a catalyst employed. The use of temperatures which, in the presence of the specific dealkylation catalyst employed, will entail any substantial amount of isomerization of the liberated 1-methylcyclopentene are, however, preferably avoided. Suitable dealkylating conditions comprise the use of sulfuric acid in the temperature range of, for example, from about 150° C. to about 200° C.

Effluence from chamber **43** comprising 1-methylcyclopentene and phenol is passed through valved line **63** into a fractionator **64**. When employing a fluid dealkylating catalyst the effluence from chamber **43** is passed through suitable catalyst removing means not shown in the drawing prior to passage into fractionator **64**. Within fractionator **64** a vapor fraction comprising 1-methylcyclopentene is separated from a liquid fraction comprising phenol. At least a part of the liquid fraction is passed through line **65** into line **46** leading into chamber **42**. A valved line **66** is provided for the elimination of a part of the recycled phenol from the system, or for its passage through suitable purifying means to avoid accumulation of any undesirable reaction products therein.

The vapor fraction consisting essentially of 1-methylcyclopentene of high purity is passed overhead from fractionator **64** through valved line **67** as a final product.

The vapor fraction comprising 4-methylcyclopentene in admixture with close boiling open chain hydrocarbons separated in fractionator **59**, is removed therefrom through line **70**. A valved line **71** is provided for the bleeding of a part of the stream from the system. Hydrocarbons thus removed from the system through valved line **71** may be subjected to conditions effecting the removal of paraffins or aromatics therefrom by means not shown in the drawing and reintroduced into line **70**.

The 4-methylcyclopentene-containing hydrocarbon stream flowing through line **70** is passed into a heating zone, such as, for example, an externally heated coil **75**, positioned in a furnace structure **76**. From coil **75** the heated hydrocarbon stream is passed through line **77** to a second olefin isomerizing zone of the process, such as, for example, a reaction chamber **78**.

Within reactor **78** the hydrocarbon stream is contacted with an olefin isomerizing catalyst at olefin isomerizing conditions effecting the conversion of 4-methylcyclopentene to cyclic olefins consisting essentially of 1-methylcyclopentene and some 3-methylcyclopentene.

Isomerization of the 4-methylcyclopentene to products comprising 1-methylcyclopentene in accordance with the invention is illustrated by the following example:

Example III

A hydrocarbon mixture consisting essentially of 4-methylcyclopentene in admixture with open chain hydrocarbons of closely approximating boiling temperatures is isomerized by contact with a bauxite catalyst at 275° C., atmospheric pressure, and a liquid hourly space velocity of 7. A conversion of 4-methylcyclopentene to 1- and 3-methylcyclopentenes of about 80% is obtained. The yield of 1-methylcyclopentene is about 60%.

Effluence from reactor **78** is passed through line **80**, provided with suitable cooling means, such as, for example, a heat exchanger **81**, into a product separating zone. The product separating zone receiving effluence from reactor **78** is depicted in the drawing by fractionators **82** and **83**.

Since the boiling temperature of 3-methylcyclopentene is 67° C. and that of the lowest boiling heptene is 72° C., separation of any 3-methylcyclopentene from the reactor effluence is easily accomplished by conventional fractionating means. Within fractionator **82** a vapor fraction comprising 3-methylcyclopentene is separated from liquid fraction comprising 1-methylcyclopentene in admixture with unconverted 4-methylcyclopentenes and close boiling heptenes and some cyclohexene.

The vapor fraction consisting essentially of 3-methylcyclopentene is taken overhead from fractionator **82** through valved line **84**. The 3-methylcyclopentene thus passed through line **84** may be taken from the system in part or entirety as a final product, or may be recycled through valved line **85** into line **70** leading into coil **75** to effect its conversion to 1-methylcyclopentene.

The liquid fraction is passed from fractionator **82** through line **86** into fractionator **83**. Within fractionator **83** a vapor fraction comprising 1-methylcyclopentene and unconverted 4-methylcyclopentenes in admixture with close boiling heptenes is separated as a vapor fraction from a liquid fraction boiling above about 84° C. comprising higher boiling materials including isomeric open chain C_7 olefins formed within the system. The liquid fraction is taken from fractionator **83** through valved line **87** and eliminated from the system. The vapor fraction comprising 1- and 4-methylcyclopentenes is recycled from fractionator **83** by means of line **90** into line **20**.

Catalysts employed in reactors **24** and **78** comprise any olefin isomerization catalyst of the solid type. Suitable solid olefin isomerization catalysts comprise, for example, the naturally occurring or synthetically prepared solid adsorptive aluminous materials, such as: the aluminum oxides, activated alumina, bauxite, silica-alumina, etc. These catalytic materials may be subjected to a pretreatment before use. Such pretreatments comprise, for example, subjection to elevated temperatures, optionally in the presence of gaseous materials such as hydrogen, nitrogen, steam, gases comprising them, or the catalysts may be contacted with an inorganic mineral acid such as hydrochloric acid, sulfuric acid, carbamic acid, hydrofluoric acid, boric acid, etc. A particularly preferred type of catalyst comprises adsorptive aluminous materials containing substantial amounts of gamma alumina which has been pretreated with an acidic material. Although adsorptive materials are preferred as catalysts for the isomerization of the 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. Of the isomerization catalysts, those consisting essentially of alumina are somewhat preferred.

Temperatures within reactors **24** and **78** are maintained in the range of from about 150° C. to about 650° C., and preferably from about 200° C. to about 350° C. Temperature conditions in reactors **24** and **78** are controlled by the heat input into the hydrocarbon streams flowing through externally heated coils **21** and **75**, respectively. The isomerization reactions are preferably executed in the vapor phase. Atmospheric, or superatmospheric pressures may be maintained within reactors **24** and **78**. Pressures close to atmospheric have been found satisfactory. Throughput rates in terms of a liquid hourly space velocity of, for example, from about 0.5 to about 25 are employed.

Under the above-defined conditions 3-methylcyclopentene is converted to cyclic olefins consisting predominantly of 1- and 4-methylcyclopentenes in reactor **24**; and 3- and 4-methylcyclopentene are converted to cyclic olefins consisting essentially of 1-methylcyclopentene in reactor **78**. Formation of undesirable by-products due to side reactions such as hydrocarbon degradation and polymerization are readily maintained at a minimum.

In a preferred modification of the invention the 1- and 4-methylcyclopentenes emanating from reactor **24** are passed from line **39** through line **95** into line **20** leading into chamber **42**, and all of the 3-methylcyclopentenes formed in reactor **78** are passed from line **84** through line **85** into line **70** to be converted to methylcyclopentenes consisting essentially of 1-methylcyclopentene in reactor **78**. In this wise substantially the entire methylcyclopentene content of the hydrocarbon charge to the system is converted to 1-methylcyclopentene and eliminated from the system as the final product through valved line **67**.

In the preferred modification of the invention isomerizing conditions within reactors **24** and **78** are preferably controlled to effect the production of methylcyclopentenes consisting essentially of 1-methylcyclopentene. Preferential formation of the 1-methylcyclopentene isomer within reactors **24** and **78** is obtained by the maintenance of relatively mild olefin isomerization conditions therein. Suitable mild isomerization conditions are obtained by the use of the lower temperatures in the prescribed broad temperature ranges and the use of the less active isomerization catalysts. Thus suitable mild isomerization conditions comprise the use of a catalyst selected from the group comprising, for example, phosphoric acid type catalysts, bauxite, sulfuric acid treated adsorptive materials, at a temperature in the range of from about 150° C. to about 350° C. Formation of cyclohexene in reactor **78** is optionally further suppressed by recycling a portion of the bottoms from fractionator **83** through valved lines **87** and **91** into line **70**.

Although the detailed illustrative description of the invention has stressed the separation of the tertiary olefin, 1-methylcyclopentene, by alkylating it with an alkylatable material, the invention is in no wise restricted to the use of this specific method of effecting the 1-methylcyclopentene separation within chamber **42**, and any of the conventional methods for effecting tertiary olefin separation from complex hydrocarbon mixtures may be resorted to in chamber **42** within the scope of the invention. Thus the hydrocarbon stream entering chamber **42** may be contacted with any suitable selectively reacting chemical agent such as sulfuric acid, halogen, hydrogen halide, etc. under conditions resulting in their selective reaction with 1-methylcyclopentene and the formation of an adduct from which the tertiary olefin, 1-methylcyclopentene, is separable in chamber **43**. The adduct may be a sulfuric acid ester, a polymer, an alcohol, a halide, an alkylate, or other adduct.

For the purpose of simplicity, all parts of apparatus not essential to a complete description of the invention, comprising, for example, pumps, condensers, complex 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 spirit and scope of the invention.

The claimed invention is:

1. The process for the production of tertiary cyclic olefins in a relatively high state of purity consisting essentially of 1-methylcyclopentene from a complex hydrocarbon mixture comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling hydrocarbons inseparable therefrom by fractionation on a practical scale, which comprises contacting said mixture with a selectively reacting chemical agent under conditions effecting the selective interaction of 1-methylcyclopentene and said chemical agent in a tertiary olefin removing zone, separating a fraction comprising the reaction products of said chemical agent and 1-methylcyclopentene and a hydrocarbon fraction comprising unconverted 4-methylcyclopentene from the effluence of said tertiary olefin removing zone, contacting said 4 - methylcyclopentene - containing hydrocarbon fraction emanating from said tertiary olefin removing zone with a solid olefin isomerization catalysts under olefin isomerizing conditions effecting the conversion of 4-methylcyclopentene to 1- and 3-methylcyclopentenes in an olefin isomerizing zone, fractionating 3-methylcyclopentene and hydrocarbons comprising 1- and 4-methylcyclopentenes from the effluence of said isomerizing zone, recycling said 3-methylcyclopentene back into said isomerizing zone, passing said hydrocarbons comprising 1- and 4-methylcyclopentenes fractionated from the effluence of said isomerizing zone to said tertiary olefin removing zone, and separating tertiary cyclic olefins in a high state of purity consisting essentially of 1-methylcyclopentene from said fraction comprising reaction products of said chemical agent and 1-methylcyclopentene separated from the effluence of said tertiary olefin removing zone.

2. The process for the production of tertiary cyclic olefins in a relatively high state of purity consisting essentially of 1-methylcyclopentene from a complex hydrocarbon mixture comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling hydrocarbons inseparable therefrom by fractionation on a practical scale, which comprises contacting said mixture with an alkylatable compound under conditions effecting the selective alkylation of said alkylatable compound with 1-methylcyclopentene in a tertiary olefin removing zone, separating a fraction comprising the alkylation products and a hydrocarbon fraction comprising unconverted 4-methylcyclopentene from the effluence of said tertiary olefin removing zone, contacting said 4 - methylcyclopentene - containing hydrocarbon fraction emanating from said tertiary olefin removing zone with a solid olefin isomerization catalysts under olefin isomerizing conditions effecting the conversion of 4-methylcyclopentene to 1- and 3-methylcyclopentenes in an isomerizing zone, fractionating 3-methylcyclopentene and hydrocarbons comprising 1- and 4-methylcyclopentenes from the effluence of said isomerizing zone, recycling said 3-methylcyclopentene back into said isomerizing zone, passing said hydrocarbons comprising 1- and 4-methylcyclopentenes fractionated from the effluence of said isomerizing zone to said tertiary olefin removing zone, and liberating tertiary cyclic olefins in a high state of purity consisting essentially of 1-methylcyclopentene from said fraction comprising alkylation products separated from the effluence of said tertiary olefin removing zone.

3. The process for the production of cyclic tertiary olefins in a relatively high state of purity consisting essentially of 1-methylcyclopentene from a complex hydrocarbon fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling hydrocarbons inseparable therefrom by fractionation on a practical scale, which comprises contacting said fraction with phenol under conditions effecting the selective alkylation of phenol with 1-methylcyclopentene in a tertiary olefin removing zone, separating a fraction comprising the alkylation product and a hydrocarbon fraction comprising unconverted 4-methylcyclopentene from the effluence of said tertiary olefin removing zone, contacting said 4-methylcyclopentene-containing hydrocarbon fraction emanating from said tertiary olefin removing zone with a solid adsorptive aluminous material under olefin isomerizing conditions effecting the conversion of 4-methylcyclopentene to 1- and 3-methylcyclopentenes in an isomerizing zone, fractionating 3-methylcyclopentene and hydrocarbons comprising 1- and 4-methylcyclopentenes from the effluence of said isomerizing zone, recycling said 3-methylcyclopentene back into said isomerizing zone, passing hydrocarbons comprising 1- and 4-methylcyclopentenes fractionated from the effluence of said isomerizing zone to said tertiary olefin removing zone, and liberating tertiary cyclic olefins in a high state of purity consisting essentially of 1-methylcyclopentene from said fraction comprising alkylation products separated from the effluence of said tertiary olefin removing zone.

4. The process for the production of cyclic olefins in a relatively high state of purity consisting essentially of methylcyclopentenes from a complex hydrocarbon mixture comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling open chain hydrocarbons inseparable therefrom by fractionation on a practical scale, which comprises contacting said hydrocarbon mixture with a selectively reacting chemical agent under conditions effecting the selective interaction of 1-methylcyclopentene and said chemical agent in a tertiary olefin removing zone, separating a fraction comprising the reaction products of said chemical agent and 1-methylcyclopentene and a hydrocarbon fraction comprising unconverted 4-methylcyclopentene from the effluence of said tertiary olefin removing zone, contacting said 4-methylcyclopentene-containing hydrocarbon fraction emanating from said tertiary olefin removing zone with a solid olefin isomerization catalyst under olefin isomerizing conditions effecting the conversion of 4-methylcyclopentene to 1- and 3-methylcyclopentenes in an isomerizing zone, fractionating 3-methylcyclopentene free of any substantial amount of open chain hydrocarbons and a hydrocarbon fraction comprising 1- and 4-methylcyclopentenes from the effluence of said isomerizing zone, passing said hydrocarbon fraction comprising 1- and 4-methylcyclopentenes fractionated from the effluence of said isomerizing zone to said tertiary olefin removing zone, and separating tertiary cyclic olefins in a high state of purity consisting essentially of 1-methycyclopentene from said fraction comprising reaction products of said chemical agent and 1-methylcy-

clopentene separated from the effluence of said tertiary olefin removing zone.

5. The process for the production of cyclic olefins in a relatively high state of purity consisting essentially of methylcyclopentenes from a complex hydrocarbon mixture comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling hydrocarbons inseparable therefrom by fractionation on a practical scale, which comprises contacting said hydrocarbon mixture with an alkylatable compound under conditions effecting the selective alkylation of said alkylatable compound with said 1-methylcyclopentene in a tertiary olefin removing zone, separating a fraction comprising the alkylation products and a hydrocarbon fraction comprising unconverted 4-methylcyclopentene from the effluence of said tertiary olefin removing zone, contacting said 4-methylcyclopentene-containing hydrocarbon fraction emanating from said tertiary olefin removing zone with a solid olefin isomerization catalyst under olefin isomerizing conditions effecting the conversion of 4-methylcyclopentene to 1- and 3-methylcyclopentenes in an isomerizing zone, fractionating 3-methylcyclopentene free of any substantial amount of open chain hydrocarbons and a hydrocarbon fraction comprising 1- and 4-methylcyclopentenes from the effluence of said isomerizing zone, passing said hydrocarbon fraction comprising 1- and 4-methylcyclopentenes fractionated from the effluence of said isomerizing zone to said tertiary olefin removing zone, and liberating tertiary cyclic olefins in a high state of purity consisting essentially of 1-methylcyclopentene from said fraction comprising alkylation products separated from the effluence of said tertiary olefin removing zone.

6. The process for the production of cyclic olefins in a relatively high state of purity consisting essentially of methylcyclopentenes from a complex hydrocarbon fraction comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling hydrocarbons inseparable therefrom by fractionation on a practical scale, which comprises contacting said hydrocarbon fraction with phenol under conditions effecting the selective alkylation of phenol with 1-methylcyclopentene in a tertiary olefin removing zone, separating a fraction comprising the alkylation products and a hydrocarbon fraction comprising unconverted 4-methylcyclopentene from the effluence of said tertiary olefin removing zone, contacting said 4-methylcyclopentene-containing hydrocarbon fraction emanating from said tertiary olefin removing zone with a solid adsorptive aluminous material under olefin isomerizing conditions effecting the conversion of 4-methylcyclopentene to 1- and 3-methylcyclopentenes in an isomerizing zone, fractionating 3-methylcyclopentene free of any substantial amount of open chain hydrocarbons and a hydrocarbon fraction comprising 1- and 4-methylcyclopentenes from the effluence of said isomerizing zone, passing said hydrocarbon fraction comprising 1- and 4-methylcyclopentenes fractionated from the effluence of said olefin isomerizing zone to said tertiary olefin removing zone, and liberating tertiary cyclic olefins in a high state of purity consisting essentially of 1-methylcyclopentene from said fraction comprising alkylation products separated from the effluence of said tertiary olefin removing zone.

7. The process for the production of tertiary cyclic olefins in a relatively high state of purity consisting essentially of 1-methylcyclopentenes from complex hydrocarbon mixtures comprising 1-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling hydrocarbons which comprises separating a lower boiling fraction comprising 3-methylcyclopentene in admixture with close boiling open chain hydrocarbons and a higher boiling fraction comprising 1- and 4-methylcyclopentenes in admixture with close boiling open chain hydrocarbons from said mixture, contacting said lower boiling fraction with a solid olefin isomerization catalyst under olefin isomerizing conditions effecting the conversion of 3-methylcyclopentene to 1- and 4-methylcyclopentenes in a first isomerizing zone, fractionating 1- and 4-methylcyclopentenes free of any substantial amount of open chain hydrocarbons from the effluence of said first isomerizing zone, contacting said higher boiling fraction with a treating agent under conditions effecting the selective removal of 1-methylcyclopentene from said higher boiling fraction in a tertiary olefin separating zone, separating a fraction comprising said treating agent and 1-methylcyclopentene and a hydrocarbon fraction comprising unconverted 4-methylcyclopentene from the effluence of said tertiary olefin separating zone, contacting said 4-methylcyclopentene - containing hydrocarbon fraction emanating from said tertiary olefin separating zone with a solid olefin isomerization catalyst under olefin isomerizing conditions effecting the conversion of 4-methylcyclopentene to 1- and 3-methylcyclopentenes in a second isomerizing zone, fractionating 3-methylcyclopentene and hydrocarbons comprising 1- and 4-methylcyclopentenes from the effluence of said second isomerizing zone, recycling said 3-methylcyclopentene fractionated from the effluence of the second isomerizing zone back into said second isomerizing zone, passing hydrocarbons comprising 1- and 4-methylcyclopentenes fractionated from the effluence of said first and second isomerizing zones to said tertiary olefin separating zone, and separating tertiary cyclic olefins in a high state of purity consisting essentially of 1-methylcyclopentene from said fraction comprising said treating agent and 1-methylcyclopentene separated from the effluence of said tertiary olefin separating zone.

8. The process for the production of tertiary cyclic olefins in a relatively high state of purity consisting essentially of 1-methyl-cyclopentene from complex hydrocarbon mixtures comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling hydrocarbons, which comprises separating a lower boiling fraction comprising 3-methylcyclopentene in admixture with close boiling open chain hydrocarbons and a higher boiling fraction comprising 1- and 4-methylcyclopentenes in admixture with close boiling open chain hydrocarbons from said mixture, contacting said lower boiling fraction with a solid olefin isomerization catalyst under olefin isomerizing conditions effecting the conversion of 3-methylcyclopentene to 1- and 4-methylcyclopentenes in a first isomerizing zone, fractionating 1- and 4-methylcyclopentenes free of any substantial amount of open chain hydrocarbons from the effluence of said first isomerizing zone, contacting said higher boiling fraction with a selectively reacting chemical agent under conditions effecting the selective interaction of 1-methylcyclopentene and said chemical agent in a tertiary olefin separating zone, separating a fraction comprising the reaction products of said

chemical agent and 1-methylcyclopentene and a hydrocarbon fraction comprising unconverted 4-methylcyclopentene from the effluence of said tertiary olefin separating zone, contacting said 4-methylcyclopentene-containing hydrocarbon fraction emanating from said tertiary olefin separating zone with a solid olefin isomerization catalysts under olefin isomerizing conditions effecting the conversion of 4-methylcyclopentene to 1- and 3-methylcyclopentenes in a second isomerizing zone, fractionating 3-methylcyclopentene and hydrocarbons comprising 1- and 4-methylcyclopentenes from the effluence of said second isomerizing zone, recycling said 3-methylcyclopentene fractionated from the effluence of said second isomerizing zone back into said second isomerizing zone, passing hydrocarbons comprising 1- and 4-methylcyclopentenes fractionated from the effluence of said first and second isomerizing zones to said tertiary olefin separating zone, and separating tertiary cyclic olefins in a high state of purity consisting essentially of 1-methylcyclopentene from said fraction comprising reaction products of said chemical agent and 1-methylcyclopentene separated from the effluence of said tertiary olefin separating zone.

9. The process for the production of cyclic tertiary olefins in a relatively high state of purity consisting essentially of 1-methylcyclopentene from complex hydrocarbon mixtures comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling hydrocarbons, which comprises separating a lower boiling fraction comprising 3-methylcyclopentene in admixture with close boiling open chain hydrocarbons and a higher boiling fraction comprising 1- and 4-methylcyclopentenes in admixture with close boiling open chain hydrocarbons from said hydrocarbon mixture, contacting said lower boiling fraction with a solid olefin isomerization catalyst under olefin isomerizing conditions effecting the conversion of 3-methylcyclopentene to 1- and 4-methylcyclopentene in a first isomerizing zone, fractionating 1- and 4-methylcyclopentenes free of any substantial amount of open chain hydrocarbons from the effluence of said first isomerizing zone, contacting said higher boiling fraction with an alkylatable compound under conditions effecting the selective alkylation of said alkylatable compound with 1-methylcyclopentene in a tertiary olefin separating zone, separating a fraction comprising the alkylation products and a hydrocarbon fraction comprising unconverted 4-methylcyclopentene from the effluence of said tertiary olefin separating zone, contacting said 4-methylcyclopentene-containing hydrocarbon fraction emanating from said tertiary olefin separating zone with a solid olefin isomerization catalyst under olefin isomerizing conditions effecting the conversion of 4-methylcyclopentene to 1- and 3-methylcyclopentenes in a second isomerizing zone, fractionating 3-methylcyclopentene and hydrocarbons comprising 1- and 4-methylcyclopentenes from the effluence of said second isomerizing zone, recycling said 3-methylcyclopentene fractionated from the effluence of said second isomerizing zone back into said second isomerizing zone, passing hydrocarbons comprising 1- and 4-methylcyclopentenes fractionated from the effluence of said first and second isomerizing zones to said tertiary olefin separating zone, and liberating tertiary cyclic olefins in a high state of purity consisting essentially of 1-methylcyclopentene from said fraction comprising alkylation products separated from the effluence of said tertiary olefin separating zone.

10. The process for the production of tertiary cyclic olefins in a relatively high state of purity consisting essentially of 1-methylcyclopentene from complex hydrocarbon mixtures comprising 1-methylcyclopentene, 3-methylcyclopentene and 4-methylcyclopentene in admixture with close boiling hydrocarbons, which comprises separating a lower boiling fraction comprising 3-methylcyclopentene in admixture with close boiling open chain hydrocarbons and a higher boiling fraction comprising 1- and 4-methylcyclopentenes in admixture with close boiling open chain hydrocarbons from said hydrocarbon mixture, contacting said lower boiling fraction with a solid adsorptive aluminous material under olefin isomerizing conditions effecting the conversion of 3-methylcyclopentene to 1- and 4-methylcyclopentenes in a first isomerizing zone, fractionating 1- and 4-methylcyclopentenes free of any substantial amount of open chain hydrocarbons from the effluence of said first isomerizing zone, contacting said higher boiling fraction with phenol under conditions effecting the selective alkylation of said phenol with 1-methylcyclopentene in a tertiary olefin removing zone, separating a fraction comprising the alkylation product and a hydrocarbon fraction comprising unconverted 4-methylcyclopentene from the effluence of said tertiary olefin removing zone, contacting said 4-methylcyclopentene-containing fraction emanating from said tertiary olefin removing zone with a solid adsorptive aluminous material under olefin isomerizing conditions effecting the conversion of 4-methylcyclopentene to 1- and 3-methylcyclopentenes in a second isomerizing zone, fractionating 3-methylcyclopentene and hydrocarbons comprising 1- and 4-methylcyclopentenes from the effluence of said second isomerizing zone, recycling said 3-methylcyclopentene fractionated from the effluence of said second isomerizing zone back into said second isomerizing zone, passing hydrocarbons comprising 1- and 4-methylcyclopentenes fractionated from the effluence of said first and second isomerizing zones to said tertiary olefin removing zone, and liberating tertiary cyclic olefins in a high state of purity consisting essentially of 1-methylcyclopentene from said fraction comprising alkylation products separated from the effluence of said tertiary olefin removing zone.

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