SYNTHESIS OF DI-TERN-BUTYLETHYLENE USING OLEFIN DISPROPORTIONATION

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Filed: Aug. 30, 1971

Appl. No.: 176,095

U.S. Cl. 260/683 D, 260/683.2
Int. Cl. C07c 3/62
Field of Search 260/683 D, 683.2

References Cited
UNITED STATES PATENTS


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ABSTRACT

Di-tert-butylethylene is prepared by contacting neohexene with an olefin disproportionation catalyst having activity for concurrent double bond isomerization. The di-tert-butylethylene is a suitable high octane component of gasoline fuels and finds particular utility in non-leaded gasolines.

10 Claims, 1 Drawing Figure
SYNTHESIS OF DI-TERT-BUTYLETHYLENE USING OLEFIN DISPROPORTIONATION

BACKGROUND OF THE INVENTION

1. Field of the Invention
This invention relates to the synthesis of high octane components of gasoline fuels. In another aspect, the invention relates to olefin disproportionation. In a still further aspect, the invention relates to the preparation of di-tet-butylethylene (2,2,5,5-tetramethyl-3-hexene).

2. Description of the Prior Art
The requirement for reduction of polluting emissions from automobile engines has placed a burden upon the oil industry to develop high quality non-leaded gasoline fuels. Thus the oil industry searches for suitable feed stock materials to provide high octane blending stocks for gasoline fuels. These are difficult to find in the so-called "gasoline pool" in current refining operations. One suitable hydrocarbon for increasing octane rating is di-tet-butylethylene (DTBE).

However, the synthesis of this material by way of an economically attractive process is difficult. In theory, one should be able to disproportionate neohexene feed material to the DTBE product. Neohexene (3,3'-dimethyl 1-butene) is structurally non-double bond-isomerizable to an internal olefin. Accordingly, one skilled in the olefin disproportionation art would predict that an olefin disproportionation catalyst, which has inherently minimal double bond isomerization activity, would provide substantial quantities of the di-tet-butylethylene product.

However, our work has shown that when neohexene is contacted with a conventional olefin disproportionation catalyst having minimal double bond isomerization activity, the neohexene converted to DTBE is very low, i.e., substantially less than about 5 percent of the product is the desired DTBE.

OBJECTS OF THE INVENTION

It is an object of this invention to synthesize di-tet-butylethylene from neohexene. It is a further object of this invention to prepare DTBE from diisobutylene. It is a still further object of this invention to synthesize DTBE from isobutene. Other objects and advantages of the invention will be apparent from the following summary of the invention, detailed description of the invention and appended claims.

SUMMARY OF THE INVENTION

We have surprisingly discovered that neohexene can be converted to high purity DTBE at high conversion and excellent selectivity by contacting the feed with an olefin disproportionation catalyst having a high degree of double bond isomerization activity even though double bond isomerization of neohexene is not apparently either required in DTBE formation or structurally possible. Nor is the product, DTBE, double bond isomerizable. Accordingly, the process of the invention comprises passing neohexene into an olefin disproportionation reactor containing a suitable olefin disproportionation catalyst which is admixed with a suitable double bond isomerization catalyst, or a solid olefin disproportionation catalyst comprising a promoter and support material wherein the support material is copromoted with a double bond isomerization promoter.

Further, in accordance with our invention we have discovered an integrated process for the preparation of de-tet-butylethylene from diisobutylene which comprises cleaving the diisobutylene with ethylene in an olefin disproportionation zone to provide neohexene. The neohexene is then converted to DTBE using the process steps mentioned above.

Further in accordance with the invention, we have discovered a unitized process for the preparation of di-tet-butylethylene from isobutene and ethylene which comprises dimerizing isobutene to diisobutylene using a suitable dimerization catalyst, cleaving the diisobutylene with ethylene in an olefin disproportionation zone to provide neohexene, and converting the neohexene to di-tet-butylethylene using the process mentioned above.

SUMMARY OF THE DRAWINGS

The sole FIGURE of the drawing is a block flow diagram illustrating the preparation of DTBE from isobutene and ethylene.

DETAILED DESCRIPTION OF THE INVENTION

The catalyst employed for the olefin disproportionation conversions utilized in our invention is any catalyst having the ability to convert propylene to ethylene and butene and to effectively isomerize 2-butene to 1-butene. Thus those olefin disproportionation catalysts which have the ability to disproportionate symmetrical internal olefins are the catalyst of choice for our process. The most suitable catalysts which have been found to effect this reaction are the combinations of a suitable double bond isomerization catalyst component and a suitable solid olefin disproportionation catalyst component. These combination catalysts are employed in a single zone as an admixture of the components or by depositing both an olefin disproportionation promoter and a double bond isomerization promoter on a single suitable support material. We prefer to use an intimate mixture of the two components because of ease of preparation of the catalyst.

It is understood that our process is not limited to the use of any particular disproportionation catalyst, double bond isomerization catalyst, or support material.

Generally, those catalysts which have been found to be particularly suitable for the conversion of neohexene are a Group II, or Group III oxide which is admixed with the disproportionation catalyst component. The Group II or Group III metal oxides employed include magnesium oxide, calcium oxide, zinc oxide, gamma-alumina, bauxite, eta-alumina, barium oxide, and strontium oxide, or mixtures thereof. Cupric phosphate supported on zinc oxide can also be used. Magnesium oxide is presently preferred because this oxide has high activity for double bond isomerization of olefins.

Any catalyst system which is capable of promoting or catalyzing the olefin disproportionation reaction of butene-2 and ethylene to propylene is suitable for use in our combination catalyst. Many of these catalysts have been reported in the prior art. Preferably, the disproportionation catalyst is one of molybdenum, tungsten, or rhenium oxide deposited on a support of silica, alumina, silica-alumina or aluminum phosphate. The mo-
lybdenum oxide-promoted catalyst is disclosed in U.S. Pat. No. 3,261,879 to Banks (1966). The tungsten oxide-promoted catalyst is discussed in U.S. Pat. No. 3,365,513 to Heckelsberg (1968). The rhenium oxide-promoted catalyst is disclosed in British Pat. No. 1,054,864 (1967), Turner et al. The disclosures of these patents are incorporated by reference. These solid catalysts can also contain minor amounts of various treating agents, such as trialkylaluminum compounds, dialkylaluminum halides, mono- and polyvalent alcohols and the like.

The disproportionation catalyst and the double bond isomerization catalyst can be modified by suitable treatment with minor amounts of an inorganic base such as alkali metal and alkaline earth metal compounds (e.g., KOH). Ordinarily, from about 0.01 to about 5 wt. percent, preferably 0.5–3 wt. percent, base is used. The catalyst can also be modified by treatment with various agents such as hydrogen, carbon monoxide, and the like. When the preferred catalyst of a mixture of WO3/SiO2 and MgO is employed, we prefer to treat the catalyst with CO at a temperature of from about 800°F to about 1,400°F for a period of time of from about 1 minute to 30 hours subsequent to activation of the catalyst mixture.

It is generally necessary to activate both the double bond isomerization and olefin disproportionation catalysts prior to use. This is generally accomplished by contact with an oxygen-containing gas at elevated temperatures, optionally followed by reduction with a modifying gas such as carbon monoxide. Activation temperatures, contact times, and other conditions of treatment have been previously reported in the art and can easily be determined by one skilled in the art.

The various suitable olefin disproportionation catalysts exhibit optimum activity within particular temperature ranges. Thus, the disproportionation steps of our invention will take place within the temperature range at which the disproportionation catalyst exhibits optimum activity. Where a mixture of the double bond isomerization catalyst and disproportionation catalyst is employed, the conversion temperature will be in the range where optimum activity for the disproportionation component occurs. Broadly speaking, the reaction temperature, depending upon the catalyst used, will be in the range of 0°–1,100°F. Using the preferred catalyst combination of MgO–WO3/SiO2, for the neohexene conversion step, we have found that a temperature in the range of from 400°F to 1,000°F is suitable, but preferably is from 650° to 800°F for optimum results.

In the conversion of neohexene to DTBE, the neohexene feed is simply contacted with the catalyst at the desired temperature and at any convenient pressure in the range of 0–2,000 psig. The neohexene can be purified prior to conversion by distillation under nitrogen followed by percolation over a mixed magnesium oxide–13X mol sieve bed at room temperature. Weight hourly space velocities can vary widely in the broad range of 0.1–1,000 WHSV, and can easily be adjusted to optimize the process.

The conversion of neohexene will primarily result in the formation of DTBE and ethylene. Some by-products are produced, such as isobutylene, dimethylbutenes, and DTBE isomers such as 2,3,4,5 tetramethyl-3,760,026 3 yl-3-hexene. The by-products can be easily separated from DTBE using conventional separation techniques, fractionation being preferred.

The neohexene can be suitably prepared by any prior art technique. However, it is preferred that the feed material be prepared by means of our invention starting from disobutylene and ethylene. Disobutylene and ethylene are contacted with a suitable olefin disproportionation catalyst to provide the primary disproportionation products of neohexene and isobutene. These primary products can be easily separated by suitable techniques. Subsequent to separation, the neohexene is contacted with the double bond isomerization catalyst and olefin disproportionation catalyst combination to provide the desired DTBE.

The catalyst of choice for the ethylene cleavage of disobutylene is the same type of combination catalyst discussed above for the neohexene disproportionation step. The proportion of ethylene to branched olefins in the feed to the ethylene cleavage unit will generally range from molar excess to about 10:1 although higher proportions of ethylene can be used if desired. Mol ratios of 3:1 are generally sufficient to achieve good results. Ethylene from the neohexene disproportionation unit is suitable for the cleavage of disobutylene and will provide some, if not all, of the ethylene required. Operating conditions such as temperature, pressure, and contact time are within the skill of one in the art and are generally the same as those reported above for the conversion of neohexene to DTBE. The principle products of the ethylene cleavage disproportionation reaction, namely neohexene and isobutene, are fundamental in that they will cleave no further with respect to the olefin disproportionation reaction. Therefore, the contact time, reaction temperature and pressure can be relatively severe without significant danger of losses due to decomposition of these materials.

The disobutylene feed to the ethylene cleavage unit can be prepared by various prior art processes or recovered from suitable disobutylene containing refinery streams. However, it is preferred that the disobutylene be prepared by a still further embodiment of my invention which comprises dimerizing isobutene to provide the disobutylene feed to the first olefin disproportionation zone, subsequently subjecting the disobutylene to disproportionation with ethylene to provide neohexene, and subjecting the neohexene to olefin disproportionation in association with a double bond isomerization catalyst to provide the di-tert-butylethylene.

The dimerization of isobutene to disobutylene can employ any suitable catalyst for this purpose. The preferred dimerization catalyst is one which will produce relatively high quantities of disobutylene (2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene) with relatively small amounts of other C9 isomers and or higher isobutene oligomers. Some examples of suitable dimerization catalysts are cold sulfuric acid; phosphoric acid on Kieselguhr; silica/alumina sometimes promoted with Ni, Co, Fe, Pt or Pd; activated natural clays plus activating substances such as ZnO; metallic phosphates such as those of iron(III) and cerium optionally supported on carriers such as activated carbon; bauxite; activated carbon alone and with metal halides such as TiCl4, heteropolyacids such as
silicotungstic acid on silica gel and phosphomolybdic acid; BF$_3$H$_4$PO$_4$ and BF$_3$HPO$_4$; dihydroxyfluoroboric acid; HF and fluorides or oxyfluorides of S, Se, N, P, Mo, Te, W, V and Si boiling below 300°C; BF$_3$-diethyl ether complexes; BF$_3$-hydrocarbon complexes; BF$_3$-SO$_3$ and AlCl$_3$ with cocatalysts such as diethyl ether, HCl, and nitromethane. These catalysts and dimerization processes, including operating conditions, are known in the art. The presently preferred catalyst is cold sulfuric acid. The preparation of DTBTE from isobutene can be understood by reference to the FIGURE of the drawing. Isobutene in line 2 is admixed with recycle isobutene from line 12 and line 22 and passed via line 13 into dimerization zone 64. Therein, contact with a suitable dimerization catalyst produces substantial quantities of diisobutylene. The effluent from the dimerization zone 64 after catalyst removal (not shown), is passed via line 3 and is admixed with ethylene from line 4 and recycle ethylene from lines 11 and 18 within line 7 prior to introduction into olefin disproportionation (DPN) zone 66. In some instances, it is desirable to subject the branched olefin effluent stream from the dimerization zone to a de-olefining step (not shown) prior to introduction into the olefin disproportionation zone 66. Within olefin disproportionation zone 66, the ethylene cleavage of diisobutylene produces neohexene and isobutene as the primary products of the reaction. Smaller amounts of propylene and heavier material are also produced and this effluent is withdrawn from zone 66 via line 8 and passed into separation zone 67. Within zone 67, separation of the zone 66 effluent provides an ethylene recycle stream 11 which is passed to line 3 via line 4. Propylene is removed from the separation area via line 9. Isobutene produced in zone 66 is removed from the separation zone 67 via line 12 and recycled to dimerization zone 64. Olefins such as unreacted diisobutylene, isoamylenes, 2,3-dimethyl-butenes, and the like are recycled to the ethylene cleavage unit via line 6 and line 7. Neohexene product is removed from the separation zone 67 via line 15. Any undesirable heavy materials can be removed via line 14. The neohexene in line 15 is passed to olefin disproportionation zone 68 wherein it is brought into contact with an olefin disproportionation catalyst and a suitable double bond isomerization catalyst. The reaction produces and effluent stream 16 containing substantial quantities of di-tert-butylethylene, other tetramethylhexenes, dimethylbutenes, isobutene, ethylene, propylene, unconverted neohexene, and other minor proportions of heavier olefin materials. The effluent in line 16 is passed to separation zone 69 wherein ethylene is removed therefrom via line 18 and returned to disproportionation zone 66. Propylene is removed via line 21. Unconverted neohexene is returned from zone 69 to disproportionation zone 68 via line 17. The dimethylbutenes are returned to zone 66 via lines 23, 6 and 7 for further conversion to neohexene. Isobutene is recycled to zone 64 via lines 22, 12 and 13 for dimerization to diisobutylene. Any undesirable heavy products can be removed from separation zone 69 by way of line 24. The DTBTE, 2,3,4,5-tetramethylhex-3-ene and 2,3,5,5-tetramethylhex-2-ene are removed from zone 69 by line 19 for further separation or for direct blending into a gasoline stock.

The drawing of the invention illustrates a simplified and generalized outline of the process of the present invention. The di-tert-butylethylene produced by our process has exceptionally good octane blending values for increasing the octane ratings of gasoline stocks. Our experiments have indicated that this material has a clear research octane blending value of about 140 in a 25 percent blend in an 80 octane reference fuel, and a clear motor octane blending value of about 130 when using the same reference fuel. Accordingly, di-tert-butylethylene containing fuels provide sufficient octane values to meet the requirements for gasoline engines requiring premium grade gasolines in the absence of tetra-alkyl lead compounds.

Our invention can be further understood by reference to the following Examples which are provided to illustrate our invention. However, the data of the Examples should not be construed as limiting the scope of the invention as disclosed herein.

**EXAMPLE I**

Neohexene was converted to di-tert-butylethylene using a tungsten oxide on silica disproportionation catalyst which was modified by various treatments, including admixture of the catalyst with suitable double bond isomerization materials.

In all runs, a heated continuous flow fixed bed reactor was employed. The feed was passed through a preheat zone prior to entry into the reactor. In those runs where the tungsten oxide on silica catalyst was employed alone, a bed of inert alpha alumina was used both above and below the tungstate catalyst as filler. In those runs where a mixed catalyst bed was employed, an inert bed of alpha alumina was positioned in the bottom of the reactor. A layer of asbestos fibers was placed above the alumina to support the mixed catalyst bed. Inert alpha alumina was also placed above the mixed catalyst.

The catalysts were activated in place by passing air through the reactor for about 3 hours at 1,000°F. The catalysts were then treated with carbon monoxide by passing the CO over them for 15 minutes at 1,000°F, and then cooled to about 650°F in the carbon monoxide atmosphere.

In those runs where the tungsten oxide on silica catalyst was base treated, a catalyst sample was added to an aqueous solution of that amount of KOH required to achieve the desired level of base on the catalyst of about 0.5g KOH per 100g WO$_3$/SiO$_2$. After about 8 minutes, the pH of the mixture indicated uptake of KOH by the catalyst. The catalyst was then separated by decantation, dried, and placed in the reactor.

In those runs where the double bond isomerization catalyst magnesium oxide was treated with KOH, the above procedure was repeated except that pH was not monitored and water was removed under reduced pressure to fix the KOH on the MgO. The amount of KOH employed in the solution was sufficient to give a desired level of base of about 1g of KOH per 100g of MgO.

The feed neohexene was distilled under a blanket of nitrogen prior to the runs, and percolated over an air actuated bed of a magnesium oxide at 135°F at ambient temperature prior to introduction into the reactor preheat zone. The conditions, catalyst compositions, and results of the runs are summarized in Table I.
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1. The same WO₃/SiO₂ composition: 6% WO₃, 22% SiO₂ possibly a trace of impurities (up to 1%) was employed in making up all of the catalysts shown here in Table I (KOH).

2. WHSB is based on WO₃/SiO₂ only. (Weight Hourly Space Velocity is equal to the grams of feed per gram of catalyst per hour.)

3. Values are for a neohexene-free basis. Abbreviations used: DMB, dimethylbutylen; DMB, dimethylbutylen; DTBE, di-tert-butylhexene; TMB, tetramethylhexene.

4. The data in Runs VI-X was a pilot-plant product used because the commercial neohexene employed in the other examples has become unavailable.

5. Ultimate yield of DTBE is equal to the moles of DTBE formed per mole of neohexene converted.
The above data clearly illustrate that a catalyst having double bond isomerization ability as well as disproportionation ability remarkably increases the conversion of neohexene to DTBE. Treatment of the combination catalyst with an alkali metal hydroxide, e.g., potassium hydroxide, generally increases the selectivity of the reaction. The ability of the catalyst combination to convert neohexene to DTBE in high yields varies with the particular double bond isomerization component which is employed, the magnesium oxide catalyst being particularly effective.

EXAMPLE II

DTBE prepared by the process of Example I was blended with the following gasoline stocks: 80 primary reference fuel, a catalytically cracked fuel, a catalytic reform fuel and a premium base fuel (51 percent catalytically cracked, 9 percent alkylate). The volume ratio of the DTBE to gasoline stock was 25:75. Results are summarized in Table II.

<table>
<thead>
<tr>
<th>Base stock, vol. percent</th>
<th>Clear blending value</th>
<th>3 ml/gal. TEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 primary ref. fuel, 100</td>
<td>80.0</td>
<td>80.0</td>
</tr>
<tr>
<td>Cat reformate, 100</td>
<td>81.4</td>
<td>74.7</td>
</tr>
<tr>
<td>Cat cracked, 100</td>
<td>87.3</td>
<td>77.8</td>
</tr>
<tr>
<td>Premium base, 100</td>
<td>91.9</td>
<td>83.6</td>
</tr>
<tr>
<td>80 primary ref. fuel, 75</td>
<td>119.2</td>
<td>119.6</td>
</tr>
<tr>
<td>Cat reformate, 75</td>
<td>124.6</td>
<td>120.9</td>
</tr>
<tr>
<td>Cat cracked, 75</td>
<td>118.1</td>
<td>117.8</td>
</tr>
<tr>
<td>Premium base, 75</td>
<td>119.9</td>
<td>96.4</td>
</tr>
</tbody>
</table>

TABLE II

1 (98.37%) 1,3-dimethylbutylethylene, 25.

We claim:

1. In a process of converting neohexene to di-tert-butyl-ethylene in the presence of an olefin disproportionation catalyst, the improvement comprising increasing the ultimate yield of di-tert-butylethylene by contacting the neohexene with a combined catalyst comprising an effective amount of a disproportionation catalyst as a first component and an effective amount of a double bond isomerization catalyst having the ability to isomerize terminal olefins to internal olefins as a second component.

2. The process of claim 1 wherein the olefin disproportionation catalyst is an oxide of molybdenum, tungsten, or rhodium deposited on a support of silica, alumina, silica-alumina, or aluminum phosphate, and the catalyst having the ability to isomerize terminal olefins to internal olefins is a Group I or Group II metal oxide, or cupric phosphate on zinc oxide.

3. The process of claim 2 wherein the olefin disproportionation catalyst is modified by treatment with an alkali metal or alkaline earth metal hydroxide.

4. The process of claim 2 wherein the olefin disproportionation catalyst is tungsten oxide on silica and the double bond isomerization catalyst is magnesium oxide.

5. The process of claim 3 wherein the olefin disproportionation catalyst is tungsten oxide on silica treated with KOH and the double bond isomerization catalyst is magnesium oxide.

6. The process of claim 1 wherein the neohexene is provided by contacting diisobutylene and ethylene with an olefin disproportionation catalyst and separating the neohexene from the effluent of the reaction of diisobutylene and ethylene.

7. The process of claim 6 wherein the diisobutylene is provided by dimerizing isobutene in the presence of a dimerization catalyst.

8. A process of preparing di-tert-butylethylene which comprises the steps of:

a. dimerizing isobutene in the presence of a dimerization catalyst to provide diisobutylene;

b. contacting the diisobutylene of steps (a) and ethylene with an olefin disproportionation catalyst to provide neohexene and isobutene;

c. separating neohexene from isobutene in the effluent from step (b) and returning the separated isobutene to step (a);

d. contacting the neohexene of step (b) with a combined catalyst comprising an effective amount of a disproportionation catalyst as a first component and an effective amount of a double bond isomerization catalyst having the ability to isomerize terminal olefins to internal olefins as a second component to provide di-tert-butylethylene and ethylene; and,

e. separating ethylene from the effluent of step (d) and returning the separated ethylene for use in step (b).

9. The process of claim 8 wherein step (d) produces isobutene and dimethylbutenes, isobutene and dimethylbutenes are separated from the effluent of step (d), the isobutene being returned to step (a) and the dimethylbutenes being returned to step (b).

10. The process of producing di-tert-butylethylene from diisobutylene and ethylene which comprises the steps of:

a. contacting diisobutylene and ethylene with an olefin disproportionation catalyst to provide neohexene and isobutene;

b. contacting the neohexene of step (b) with a combined catalyst comprising an effective amount of a disproportionation catalyst as a first component and an effective amount of a double bond isomerization catalyst having the ability to isomerize terminal olefins to internal olefins as a second component to provide di-tert-butylethylene and ethylene; and,

c. returning the ethylene of step (b) to step (a).

... * * * *