

[54] **PREPARATION OF POLYPHENYLS** 3,209,042 9/1965 Scola 260/668 D
2,658,089 11/1953 Ipatieff..... 260/668 D

[75] **Inventor:** Robert M. Suggitt, Wappingers Falls, N.Y.

[73] **Assignee:** Texaco Inc., New York, N.Y.

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[52] **U.S. Cl.** 260/668 D; 260/668 R

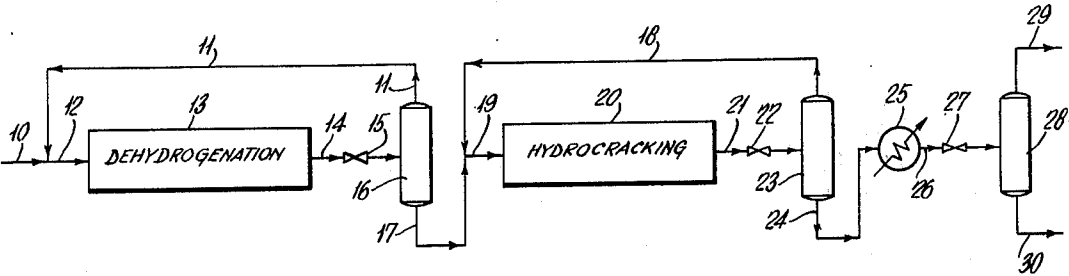
[51] **Int. Cl.²** C07C 15/14

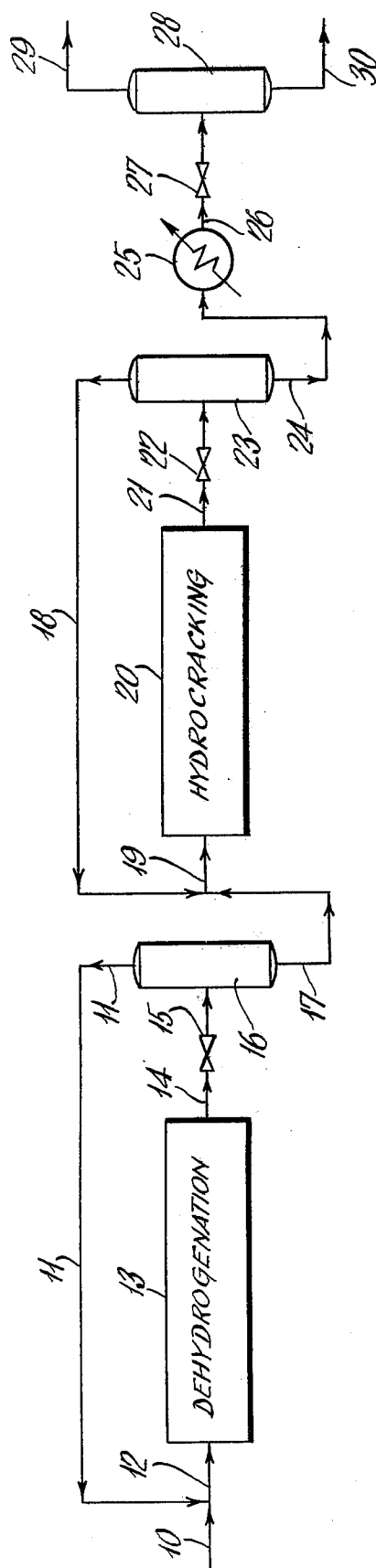
[58] **Field of Search**..... 260/668, 668 D

[56] **References Cited**
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[57] **ABSTRACT**
Cyclohexyl benzenes may be selectively dehydrogenated to yield aromatics; by-products may be selectively removed by cracking.

18 Claims, 1 Drawing Figure





PREPARATION OF POLYPHENYLS

BACKGROUND OF THE INVENTION

This invention relates to the preparation of polyphenyls by selective dehydrogenation of cyclohexyl benzenes. More particularly this invention relates to the dehydrogenation of products of hydroalkylation to form desired aromatic hydrocarbons.

As is well known to those skilled in the art, higher molecular weight aromatics, typified by biphenyls and terphenyls may be difficult to prepare in high purity because of their high boiling point which precludes distillation at reasonable temperatures and pressures. Among the techniques used to recover such materials may be noted vacuum distillation, crystallization, etc. It may be difficult to attain these materials in high purity because many techniques by which they may be recovered, give undesirable yields of by-products or require very severe processing conditions.

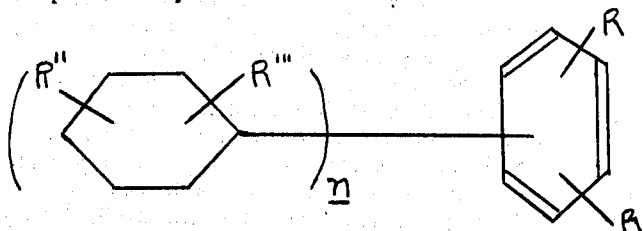
It is an object of this invention to provide a process for preparing selected aromatic hydrocarbons. It is a further object of this invention to provide a process for dehydrogenating a cyclohexyl benzene to form aromatic components and to permit recovery of these aromatic components. Other objects will be apparent to those skilled in the art.

STATEMENT OF THE INVENTION

In accordance with certain of its aspects, the novel method of this invention may comprise dehydrogenating a naphthenyl benzene in a non-oxidative atmosphere at dehydrogenation conditions in the presence of non-acidic dehydrogenation catalyst thereby forming a dehydrogenated stream containing desired aromatic components; and recovering said desired aromatic components.

DESCRIPTION OF THE INVENTION

The charge naphthenyl benzene hydrocarbons which may be treated by the process of this invention may be characterized by the presence of an aromatic ring and at least one naphthenyl cyclohexyl ring. Typically the charge cyclohexyl benzene charge hydrocarbons may be represented by the formula:



In the above formula n may be an integer 1-4 preferably 1 or 2. R , R' , R'' , and R''' may be hydrogen or lower alkyl; when R , R' , R'' , or R''' is lower alkyl, it may preferably be methyl or ethyl.

In a preferred embodiment, the naphthenyl cyclohexyl group and the aromatic benzene ring may contain the same number of carbon atoms and may possess the same configuration. For example, if the naphthenyl moiety is cyclohexyl, the aromatic moiety may be phenyl; if the naphthenyl moiety is methylcyclohexyl, the aromatic moiety may be tolyl; etc.

Typical examples include where $n = 1$ cyclohexylbenzene, methylcyclohexyl toluenes (12 isomers),

(ethylcyclohexyl) ethyl benzenes, (dimethylcyclohexyl) xylenes, etc;

Where $n = 2$

para-dicyclohexylbenzene
meta-dicyclohexylbenzene
ortho-dicyclohexylbenzene
dicyclohexyl toluenes
di(ethylcyclohexyl) ethylbenzenes
(methylcyclohexyl)cyclohexylbenzene
di(methylcyclohexyl) toluenes
di(dimethylcyclohexyl) xylenes

$n = 3$

1,3,5-tricyclohexylbenzene
1,2,4-tricyclohexylbenzene
tri(methylcyclohexyl) toluenes
tri(ethylcyclohexyl) ethylbenzenes

Mixtures of (substituted cyclohexyl) substituted benzenes can be formed by hydroalkylating substituted benzene. For example the hydroalkylation of benzene results in a mixture that contains (aside from unreacted benzene) cyclohexylbenzene, dicyclohexylbenzenes (para, meta, and ortho isomers) and tricyclohexylbenzenes.

The hydroalkylation of toluene forms a mixture containing (methylcyclohexyl) toluenes, di(methylcyclohexyl) toluenes, and tri(methylcyclohexyl) toluenes.

In hydroalkylating xylenes, (dimethylcyclohexyl) xylenes and di(dimethylcyclohexyl) xylenes and tri(dimethylcyclohexyl) xylenes are formed.

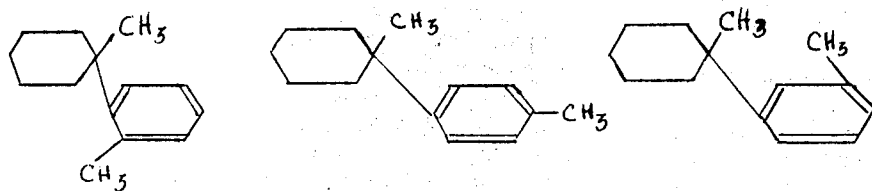
When mixtures of aromatics, such as benzene and toluene or C_6-C_8 aromatics are hydroalkylated, additional compounds may be formed such as:

cyclohexyl toluenes
(methylcyclohexyl) benzenes
methylcyclohexyl cyclohexyl toluenes
methylcyclohexyl cyclohexyl benzenes
di(methyl cyclohexyl) benzenes
dicyclohexyl toluenes
cyclohexyl xylenes
cyclohexyl ethylbenzenes
methylcyclohexyl xylenes
(ethyl cyclohexyl) xylenes
di(ethylcyclohexyl) xylenes

di(dimethylcyclohexyl) ethylbenzenes
(ethylcyclohexyl) (dimethylcyclohexyl) ethylbenzene
(ethylcyclohexyl) (dimethylcyclohexyl) xylenes
(ethylcyclohexyl) cyclohexyl toluenes
(ethylcyclohexyl) cyclohexyl benzenes
(ethylcyclohexyl) cyclohexyl xylenes

While a large number of isomers of (substituted cyclohexyl) substituted benzenes can be formed by hydroalkylation many of these isomers occur, if at all, in very low concentrations. In particular the formation of isomers where an alkyl group is substituted on the same carbon that bonds the cyclohexyl group to the benzene

ring are sterically not favored during hydroalkylation. For example, when hydroalkylating toluene, the formation of the following isomers is not favored because of steric factors:



It is a feature of the process of this invention that such compounds as these are not preferred charge materials.

Similarly it is understood that when the (dimethylcyclohexyl) benzenes, (dimethylcyclohexyl) toluenes, and (dimethylcyclohexyl) xylenes are formed by hydroalkylating an aromatic containing xylenes, the two methyl groups on the cyclohexyl ring are not attached to the same carbon. That is, the carbon in the cyclohexyl ring to which a methyl group is attached must also have a hydrogen substituent to permit the facile dehydrogenation of the cyclohexyl ring.

It is a feature of the process of this invention that the hydroalkylating reaction does not favor the formation of such undesirable compounds as described above. Thus the hydroalkylating reaction is ideally suited for the preparation of the feed materials for the process of this invention.

It is to be appreciated that other compounds can be formed in minor amounts during the hydroalkylation. Some, such as bicyclohexyl or other substituted bicyclohexyls, are suitable feed material for the subject process. However, most byproducts of the reaction do not contribute substantially to the desired products.

For example, during the hydroalkylation of benzene, (methylcyclopentyl) benzenes are formed which possess physical properties similar to cyclohexylbenzene and hence are difficult to separate from the cyclohexylbenzene. Likewise, the dicyclohexylbenzene distillate fraction contains impurities such as (methylcyclopentyl) cyclohexylbenzenes. While the dicyclohexylbenzenes are preferred materials for forming terphenyls, the impurities do not generate terphenyls, although some biphenyls can be formed if the methylcyclopentyl group can be cracked off.

In addition, when hydroalkylating benzene, cyclohexane and methylcyclopentane are also formed.

Similar cyclopentyl impurities are formed in hydroalkylating toluene, xylenes, and ethyl benzenes or mixtures thereof with or without benzene.

In addition, naphthenes corresponding to the feed aromatic are also formed during hydroalkylation. Thus, for example, cyclohexane and methylcyclopentane are formed during the hydroalkylation of benzene. Likewise methylcyclohexane and dimethylcyclopentanes are generated during the hydroalkylation of toluene; dimethylcyclohexanes and trimethylcyclopentanes in hydroalkylation of xylenes; and ethylcyclohexane and methylethylcyclopentanes in hydroalkylation of ethylbenzene.

These saturated naphthenes are inert under hydroalkylation conditions. That is, cyclohexane does not react with benzene to make cyclohexylbenzene. It has been heretofore necessary then to eventually separate these naphthenes from the charge aromatic and then dispose of them.

It is a feature of the process of this invention that these saturated naphthenes may be included in the (substituted cyclohexyl) substituted benzene feed either for dehydrogenation back to the parent aromatic

as in the case of the cyclohexane derivatives or for cracking to light product as in the case of the cyclopentane derivatives. In either event, their inclusion in the feed to the process of the invention together with non-hydroalkylated aromatic, eg benzene, toluene, xylenes, or ethylbenzene, can provide a means of reconcentrating or purifying the feed aromatic prior to recycling the aromatic back to the hydroalkylation reactor.

The particular composition of the feed to dehydrogenation will be dictated by the products desired. For example, if para-terphenyl is desired, then the feed should contain para-dicyclohexylbenzene such as may be provided either as a mixture or with further purification (eg as by the processes disclosed in U.S. Pat. Nos. 3,784,617 or 3,784,618 or 3,784,619. Likewise to make meta-terphenyl, the feed should contain meta-dicyclohexylbenzene.

Biphenyl and terphenyls may be made simultaneously by employing as feedstock a mixture containing cyclohexylbenzene and dicyclohexylbenzenes.

The effluent from a hydroalkylation unit may be used, with or without further separation depending on the polyphenyl products desired. The total hydroalkylation effluent (hydrogen + hydrocarbons) may be heated up, and optionally combined with additional hydrogen, and passed to the dehydrogenation operation.

In practice of the process of this invention according to certain of its aspects, the charge cyclohexyl benzene may be dehydrogenated in a non-oxidative atmosphere at dehydrogenation catalyst containing at least one metal selected from the group consisting of rhenium, Group VI B metals, and Group VIII metals thereby forming a dehydrogenated stream containing (i) desired aromatic components and (ii) undesired components having a naphenyl-aromatic bond.

The non-oxidative atmosphere in which the process of this invention may be carried out may be the autogenous atmosphere generated during the reaction. In another embodiment, the atmosphere may contain 0-50, typically 1-20, say 3 moles (per mole of charge) of hydrogen admitted with the hydrocarbon charge. Inert diluents such as nitrogen, steam, etc. may be present in amount of 0-100 moles, typically 1-20 moles, say 2 moles per mole of hydrocarbon charge.

In one preferred embodiment, there may be admitted with the charge at least a portion of the recycled product stream either before or after the latter is purified.

Dehydrogenation is carried out at dehydrogenation conditions including a temperature of 700°-1100°F, preferably 750°-1000°F, say 875°F and at a total pressure of 0-1000 psig, preferably 50-300 psig, say 75 psig.

Reaction may be carried out in the presence of a non-acidic catalyst. Catalyst supports which may be employed as non-acidic supports include neutral and

basic supports. Typically such supports contain basic moieties in their structure (including groups adsorbed thereon) or they may be neutral. In preferred embodiments, they may be pretreated with aqueous caustic (eg sodium hydroxide or more preferably potassium hydroxide) and calcined. Typical of such supports are base-leached carbon, caustic washed alumina, potassium hydroxide-treated alumina, silica gel, etc. A typical alumina may contain 0.5% Li₂O or 1.5% K₂O.

A non-acidic alumina can be distinguished from an acidic alumina by contacting a sample of the freshly calcined alumina (5 hours at 500°C) with a solution of dry benzene saturated with phenolphthalein. When so contacted, non-acidic aluminas remain colorless, while acidic aluminas form a red color of a shade distinctly different from the well known purple color of phenolphthalein in basic media. Adding water to the red colored dry alumina impregnated with phenolphthalein causes a slow fading of color in the case of truly acidic alumina. When water is added to colorless samples of basic aluminas (those containing sizable amounts of alkali) impregnated with phenolphthalein an intense purplish red color develops in the water layer.

There may be deposited on and within the support at least one metal selected from the group consisting of rhenium Re, a Group VI B metal, and a Group VIII metal. When the metal is a Group VI B metal, it may be chromium Cr, molybdenum Mo, or tungsten W. When the metal is a Group VIII metal it may be iron Fe, cobalt Co, or nickel Ni or more preferably a noble metal including ruthenium Ru, rhodium Rh, palladium Pd, iridium Ir, or platinum Pt. The preferred metal may be a metal of Group VIII, preferably platinum, or a combination of Group VIII platinum metals such as Pt-Ir.

When more than one metal is present, it may be eg nickel-chromium; but more preferably it is preferred that it be a Group VIII noble metal plus a Group VI B Metal: eg platinum-molybdenum, platinum-rhenium, etc. When the metal is nickel or cobalt, it is particularly preferred that a Group VIB metal be present.

The catalyst may contain the metal (when the metal is cobalt or nickel) in amount of 2-15 parts, preferably 3-10 parts, say 5 parts per 100 parts of support. When the metal is a Group VI B metal it may be present in amount of 5-40 parts, preferably 10-30 parts, say 20 parts (eg of Cr₂O₃ or Mo₂O₃) per 100 parts of support.

The catalyst may be typically prepared, in one embodiment, by contacting a low ash activated carbon in an impregnating solution containing potassium carbonate and ammonium chloroplatinate in sufficient amounts to provide 1.0% K₂O and 0.8 percent platinum on drying. The catalyst may then be calcined in an non-oxidizing atmosphere, eg in nitrogen at 500°C.

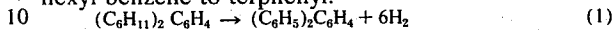
Alternatively, in another typical embodiment, a catalyst may be prepared by impregnating an alumina with a solution containing potassium nitrate and ammonium molybdate in sufficient amounts to provide a composition on drying and calcining that contains by weight 1.5% K₂O and 20% Mo₂O₃.

The catalyst may be activated by contact with flowing hydrogen at 700°-1100°F, preferably 750°-1000°F, say 875°F.

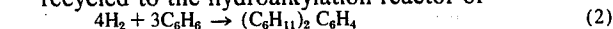
In accordance with practice of the process of this invention, dehydrogenation may be effected to convert the cyclohexyl aromatic to a desired aromatic component in which the product cyclohexyl-derived moiety contains less hydrogen than does the charge cyclohexyl

moiety. In the preferred embodiment, the charge cyclohexyl moiety is selectively converted to high yields of aromatic moiety — and in typical operation, the charge cyclohexyl moiety may be selectively converted to aromatic moieties in conversion of 30-100%, preferably 50-100%, say 70%.

During dehydrogenation, the following typical reaction may occur in the case of the conversion of dicyclohexyl benzene to terphenyl:



It may be noted that during hydroalkylation of benzene to produce the typical charge stream to the process of this invention, four net moles of hydrogen are used to make dicyclohexylbenzene when it is assumed that the intermediate product cyclohexylbenzene is recycled to the hydroalkylation reactor or



It is then to be noted that, by combining the hydroalkylation reaction of benzene (2) with the dehydrogenation of the cyclohexylbenzene (1), in theory there is a net gain of hydrogen. Overall adding reaction (2) to reaction (1), the result is $3 C_6H_6 \rightarrow (C_6H_5)_2 C_6H_4 + 2 H_2$. In practice, side reactions consume hydrogen and a net gain of hydrogen is not experienced. However, it is to be noted that overall hydrogen consumption is minimal and no environmentally undesirable side products are generated.

Furthermore in generating biphenyl, overall yields can be high, hydrogen consumption minimal, by using relatively mild processing conditions.

The product stream may typically contain desired aromatic components containing less hydrogen than does the charge component and thus possessing a higher degree of unsaturation. In the preferred embodiment, the cyclic moieties in the product will contain a higher degree of aromatic unsaturation. In the case of dehydrogenation of eg cyclohexyl benzene, the product stream will contain the desired phenyl benzene (i.e., biphenyl). In the case of dehydrogenation of dicyclohexyl benzene, the product stream will contain the desired diphenyl benzene (i.e., terphenyl) — the latter compound is particularly useful as a heat transfer medium.

The product stream will also contain undesired naphthenyl aromatic components. In the case of dehydrogenation of cyclohexyl benzene, the product stream may contain undesired unconverted cyclohexyl benzene plus undesired benzene and methylcyclopentylbenzenes. In the case of charge dicyclohexyl benzene, the undesired components in the product stream may include cyclohexyl, phenyl benzene; dicyclohexenyl benzene; cyclohexyl, cyclohexenyl benzene; (methylcyclopentyl) phenylbenzene etc.

It is a feature of the process of this invention that unexpectedly the reaction conditions which are conducive to dehydrogenation of the cyclohexyl moiety in the charge cyclohexyl aromatic hydrocarbon desirably give little or no cracking of the cyclohexyl aromatic bond. Typically less than 30 wt % of the charge is cracked by rupture of this bond.

When dehydrogenating a crude stream recovered for example from the hydroalkylation of benzene which may contain a mixture including benzene, cyclohexane, cyclohexylbenzene methylcyclopentylbenzene, dicyclohexylbenzenes, (methylcyclopentyl) cyclohexyl benzene, etc., the dehydrogenation product mixture may contain:

benzene

methylcyclopentane
cyclohexane
biphenyl
methylcyclopentylbenzenes
methylcyclopentenylbenzenes
methylcyclopentadienylbenzenes
trace amounts of cyclohexylbenzene
terphenyls
cyclohexyl phenyl benzenes
(methylcyclopentyl), phenyl benzenes
dicyclohexylbenzenes

Biphenyl and the terphenyls present may be recovered from the above mixture by fractionation and then purified. Biphenyl and terphenyls may be recovered by crystallization of these distillate cuts.

The high boiling residues (higher boiling than benzene) from these recovery steps may in part be recycled to the dehydrogenation reactor to effect further conversion of species such as unreacted cyclohexylbenzene and dicyclohexylbenzenes. A portion, however, should be drawn off and discarded or preferably cracked at high temperatures to recover benzene and biphenyl.

With mixtures of (substituted cyclohexyl) substituted benzenes (such as formed by hydroalkylating toluene, xylene or ethylbenzene), it will be appreciated that the number of possible bi(substituted phenyl) and ter(substituted phenyls) products is large; and the mixed biphenyls or mixed ter(substituted phenyls) can not be readily separated from unreacted species of similar boiling range by means of crystallization techniques alone.

It is a feature of this invention that these desired poly(substituted phenyls) can be purified of naphthenyl derivatives by cracking the naphthenyl groups.

In practice of the process of this invention, the dehydrogenated stream as withdrawn from dehydrogenation (and in the preferred embodiment with no intermediate treatment except possibly separation of recycle hydrogen) may be cracked (e.g. hydrocracked) at cracking conditions. When this stream is cracked, it may be cracked at 500°–1100°F, preferably 700°–1100°F, say 875°F. When the stream is hydrocracked, this may be effected at 500°–900°F, preferably 600°–800°F, say 700°F at 50–2000 psig, preferably 200–1000 psig, say 750 psig.

Hydrocracking may be carried out in liquid phase over an acidic catalyst containing at least one metal selected from the group consisting of rhenium, Group VI B metals, and Group VIII metals. The catalyst metals may preferably be in a sulfided form, and preferably be supported on an acidic support such as alumina, silica-alumina, acid zeolites, etc. The catalyst may be prepared by impregnating an acidic catalyst (such as (i) alumina, preferably fluorided with 1–10%, say 3–6% fluoride, with ammonium fluoride and then calcined or (ii) silica-alumina, or (iii) magnesium, calcium, or rare earth exchanged zeolites) with nickel and molybdenum. When cracking is not done in the presence of added hydrogen, preferred catalyst may be silica-alumina; or magnesium, calcium or rare earth exchanged zeolite at 700°–1100°F.

Preferably a light aromatic stock such as one containing benzene or toluene may be included in the feed-stock to the cracking reaction to assist in removal of the polyphenyl product; such a diluent may help to wash off the strongly sorbed biphenyl or ter(substituted phenyl(s)) from the catalyst.

It is a feature of the process of this invention that mild cracking will rupture the naphthene-to-aromatic bond(s) in the undesired components without rupturing the aromatic-aromatic bonds in the desired components. In the case of charge dicyclohexyl benzenes which have been dehydrogenated to desired terphenyl and which contain eg unconverted dicyclohexyl benzenes, the latter are cracked to a lower boiling fraction containing benzene, toluene, and light olefins.

This difference in boiling point makes it readily possible to separate the desired products from the undesired products as by distillation or by flashing in the case of poly(substituted phenyl compounds). Such a separation is not readily or conveniently possible in the case of the uncracked stream because the boiling ranges of the desired poly(substituted phenyl) compounds and those of the undesired naphthenyl aromatics may overlap.

In the case of the charge dicyclohexyl benzenes, the product (ex hydrogen) leaving cracking or hydrocracking may typically contain 60 parts of terphenyls, 30 parts biphenyls, 5 parts of benzene, 3 parts of toluene, 2 parts of ethylbenzene, and 15 parts of light hydrocarbons including olefins, C₁ to C₄ paraffins, etc.

In practice of the process of this invention, the cracked product may be passed to separation. Although this may be carried out in a distillation column, it is a feature of this invention that desired aromatic components may be readily separated from the undesired lower boiling products in the stream recovered from cracking, by flashing off light components; and the eg bi-phenyl an terphenyls may be separated by distillation.

This process may be useful to prepare a wide variety of aromatics products (in good purity and yield) which could only be attained less conveniently, if at all, by other possible processes eg tolyl toluenes typified by para (para-tolyl) - toluene; terphenyl; 1,3,5-triphenyl benzene; meta-tolyl benzene; etc.

It is particularly unexpected that one should be able to selectively operate in manner (a) to dehydrogenate without cracking, thereafter (b) to be able to selectively crack the undesired components without destruction of the desired components, and (c) to then easily separate the desired components.

Practice of the process of this invention will be apparent to those skilled in the art from inspection of the following wherein, as elsewhere in this application, all parts are parts by weight unless otherwise stated.

EXAMPLE I

a. In this example which represents a preferred embodiment of the process of this invention, dehydrogenating catalyst may be prepared by immersing 100 parts of gamma alumina (1.5 mm average diameter pellets) in 70 parts of 2.9% aqueous solution of potassium hydroxide for 4 hours, drying at 200°F for 4 hours, and calcining at 900°F for 5 hours to yield a non-acidic alumina support containing 1.65% K₂O. The support is then cooled to ice temperature and immersed in 70 parts of chilled aqueous solution of chloroplatinic acid containing 1.5 parts of platinum to which 2.6 parts of ethylene diamine have been added. The amount of solution is sufficient to give a slight excess of liquid over that needed to wet the pellets and thus insure uniform wetting of the pellets. After standing for 1 hour, the catalyst is dried at 225°F for 2 hours and then heated successively for one hour each at 500°F, 600°F,

and 750°F, and finally for 2 hours of 1050°F.

b. Dehydrogenating may be carried out by passing dicyclohexyl benzenes (100 parts containing 30 parts of para-dicyclohexyl benzene, 65 parts of ortho- and meta-isomers, and 5 parts of dinaphthenyl benzenes boiling in the dicyclohexyl benzene range) at 850°F and 50 psig into contact with the catalyst. 100 parts of benzene diluent is admitted with the charge. LHSV of the charge dicyclohexyl benzene plus benzene is 3; and 4 moles of hydrogen are admitted per mole of charge dicyclohexyl benzene.

The product from dehydrogenation may include 7 parts of unconverted dinaphthenyl benzenes, 57 parts of terphenyls, 9.5 parts of biphenyl, and 8 parts of other mono-naphthenyl and alkyl aromatics.

c. The dehydrogenated product may be fractionated to yield a light material (primarily benzene), a middle cut (boiling at 450°–500°F containing biphenyl), and a bottoms containing terphenyl. The middle cut may be cooled to ambient temperature, typically 80°F, to form crystals of biphenyl which can be separated and purified by recrystallization from ethanol. The bottoms (boiling above about 500°F) may be purified by cooling to form solid crystals and recrystallizing from ether or acetic acid.

Preferably the dehydrogenated product may be flashed to remove the light materials and the remainder passed to a cracking operation wherein it is cracked over an acidic silica-alumina catalyst.

d. Cracking is effected at 850°F and 0 psig to yield a product containing 15 parts of light hydrocarbons, 915 parts light aromatics added as diluent (benzene, toluene, and C₈ aromatics), 55 parts terphenyls, and 10 parts biphenyl.

Results comparable to those achieved in Example I may be obtained by the following:

EXAMPLE II

The process of Example I may be carried out except that the dehydrogenation catalyst may contain unsupported zinc chromite (a non-acidic catalyst) containing 1 mole of ZnO per 1 mole of Cr₂O₃.

EXAMPLE III

The process of Example I may be carried out using as the charge naphthenyl aromatic hydrocarbon - cyclohexyl benzene and producing biphenyl.

EXAMPLE IV

An impure "toluene dimer" stock was prepared from toluene (which had been dried over silica gel) by hydroalkylation. The catalyst contained (i) 78% amorphous silicaalumina matrix within which was dispersed (ii) 22% of hydrogen Y zeolite containing 4% nickel. Hydroalkylation was carried out at inlet temperature of 320°F, exit temperature of 406°F, pressure of 473 psig, 3 LHSV, and complete consumption of hydrogen admitted (1.8 parts per 100 parts of toluene). The product contained 0.57% dimethylcyclopentane, 13.16% methylcyclohexane, 18.0% toluene dimers i.e. methylcyclohexyl toluenes, 0.62% toluene trimers i.e. di(methylcyclohexyl) toluenes, and the remainder, toluene.

The toluene dimers contain methylcyclohexyl toluenes and dimethylcyclopentyl toluenes. The toluene trimers contain di(methylcyclohexyl) toluenes and other dinaphthenyl toluenes.

The toluene dimers may be recovered by fractionating to recover the material boiling at 500°–600°F.

These dimers may be dehydrogenated over a catalyst prepared by impregnating ammonium molybdate solution onto alumina pellets containing 1% sodium. The impregnated catalyst, containing 14% molybdenum, is dried for 5 hours at 220°F and calcined for 4 hours at 930°F in a stream of hydrogen at atmospheric pressure.

The toluene dimer may then be introduced at LHSV of 0.5 at 900°F and 200 psig with a hydrogen to toluene dimer mole ratio of 6:1. The dehydrogenated product is passed, without any separation, to a cracking operation at atmospheric pressure and 900°F. The catalyst is a rare earth exchanged zeolite cracking catalyst. The cracked effluent product contains light hydrocarbons, toluene, and bitolyls that boil between 490° and 565°F.

EXAMPLE V

The process of Example IV may be carried out except that cracking is carried out at hydrocracking conditions including inlet temperature of 650°F, pressure of 500 psig, over an acidic catalyst containing 12% MoS₂ on silica-alumina.

EXAMPLE VI

The process of Example I may be carried out except that the dehydrogenation catalyst may contain 1% palladium on a low ash activated carbon.

EXAMPLE VII

Practice of the process of this invention may be apparent by reference to the drawing which schematically shows a flow sheet according to which the process may be carried out.

In the drawing, there may be admitted through line 10, a dicyclohexyl benzene charge in amount of 100 parts containing 30 parts of para-isomer and 65 parts of ortho- and meta-isomers, and 5 parts of dinaphthenyl) benzene boiling in the dicyclohexyl benzene range. 4 moles of hydrogen per mole of charge dicyclohexyl benzene are admitted through line 11 and the mixture admitted through line 12 to dehydrogenation operation 13 at LHSV of 3. Catalyst in operation 13 is platinum on (non-acidic) gamma alumina prepared as in Example I supra. Dehydrogenation is effected at inlet temperature of 800°F and pressure of 50 psig.

Effluent is preferably passed through line 14, and valve 15 to separation operation 16. Hydrogen may be separated and recycled to charge in line 10.

Dehydrogenated product in line 17 may be mixed with hydrogen (the hydrogen being admitted through line 18) and the mixture passed through line 19 to hydrocracking operation 20. The catalyst in hydrocracking operation 20 may be 5% cobalt sulfide on rare earth exchanged zeolite. Inlet temperature in line 19 is 675°F at 300 psig.

Effluent from hydrocracking in line 21 may be passed through line 21 and valve 22 to separation operation 23 wherein hydrogen may be separated and recycled to the charge to hydrocracking. The effluent (ex. hydrogen) may contain terphenyl, biphenyl, light aromatics added as diluent (eg benzene), light hydrocarbons (eg cyclohexane) etc.

Hydrocracked product in operation 23 may be withdrawn through line 24, heated in heat exchanger 25, passed through line 26 and valve 27, and flashed in flash drum 28.

Overhead removed through line 29 may contain the light components and the desired product terphenyl may be recovered in amount of about 55 parts of sub-

stantially pure product.

It will be apparent to those skilled in the art that the drawing is schematic; and that various pumps, heat exchangers, collection vessels, etc. are not specifically shown.

Although this invention has been illustrated by reference to specific embodiments, it will be apparent to those skilled in the art that various changes and modifications may be made which clearly fall within the scope of this invention.

I claim:

1. The method which comprises dehydrogenating a naphthenyl benzene in a non-oxidative atmosphere at dehydrogenation conditions in the presence of non-acidic dehydrogenation catalyst thereby forming a dehydrogenated stream containing desired aromatic components; and recovering said desired aromatic components.

2. The method claimed in claim 1 wherein said dehydrogenation is carried out at 700°–1100°F.

3. The method claimed in claim 1 wherein said catalyst includes at least one metal selected from the group consisting of rhenium, Group VI B metals, and Group VIII metals.

4. The method claimed in claim 1 wherein said catalyst includes a Group VIII metal.

5. The method claimed in claim 1 wherein said catalyst includes a non-acidic support.

6. The method claimed in claim 1 wherein said catalyst includes a Group VIII metal on non-acidic alumina.

7. The method claimed in claim 1 wherein said naphthenyl benzene is cyclohexyl benzene.

8. The method claimed in claim 7 wherein said naphthenyl benzene is a dicyclohexyl benzene.

9. The method which comprises dehydrogenating a dicyclohexyl benzene in a non-oxidative atmosphere at dehydrogenation conditions including pressure of 0–1000 psig and temperature of 700°–1100°F in the presence of a non-acidic dehydrogenation catalyst containing a Group VIII metal on a non-acidic support thereby forming a dehydrogenated stream containing terphenyl; and recovering said terphenyl.

10. The method claimed in claim 9 wherein said temperature is 750°–1000°F.

11. The method which comprises dehydrogenating a naphthenyl benzene in a non-oxidative atmosphere at dehydrogenation conditions in the presence of non-acidic dehydrogenation catalyst thereby forming a dehydrogenated stream containing (i) desired aromatic components and (ii) undesired components having a naphthenyl-aromatic bond;

cracking said dehydrogenated stream at cracking conditions thereby rupturing at least a portion of

said naphthenyl-aromatic bonds and forming lower boiling products;

separating said lower boiling products; and recovering said desired aromatic components.

12. The method claimed in claim 11 wherein said cracking is hydrocracking.

13. The method claimed in claim 11 wherein said cracking is carried out in the presence of acidic catalyst.

14. The method claimed in claim 11 wherein said cracking is carried out in the presence of a Group VIII metal on a silica-alumina.

15. The method claimed in claim 11 wherein said cracking is cracking carried out at 700°–1100°F.

16. The method claimed in claim 11 wherein said naphthenyl benzene contains at least one component selected from the group consisting of cyclohexyl benzenes and dicyclohexyl benzenes.

17. The method which comprises dehydrogenating a naphthenyl benzene in a non-oxidative atmosphere at dehydrogenation conditions including pressure of 0–1000 psig and temperature of 700°–1100°F in the presence of a non-acidic dehydrogenation catalyst containing at least one metal selected from rhenium, Group VI B metals, and Group VIII metals thereby forming a dehydrogenated stream containing (i) desired aromatic components and (ii) undesired components having a naphthenyl-aromatic bond;

hydrocracking said dehydrogenated stream at cracking conditions including temperature of 500°–800°F and 50–2000 psig thereby rupturing at least a portion of said naphthenyl-aromatic bonds and forming lower boiling products;

separating said lower boiling products; and recovering said desired aromatic components.

18. The method which comprises dehydrogenating a charge stream containing dicyclohexyl benzene in a non-oxidative atmosphere at dehydrogenation conditions including pressure of 0–1000 psig and temperature of 700°–1100°F in the presence of a non-acidic dehydrogenation catalyst containing at least one metal selected from rhenium, Group VI B metals, and Group VIII metals thereby forming a dehydrogenated stream containing (i) desired terphenyl and (ii) undesired components having a naphthenyl-aromatic bond;

hydrocracking said dehydrogenated steam at cracking conditions including temperature of 500°–800°F and 50–2000 psig in the presence of an acidic catalyst thereby rupturing at least a portion of said naphthenyl-aromatic bonds and forming lower boiling products;

separating said lower boiling products; and recovering said desired terphenyl.

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