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PRODUCTION OF CYCLOOLEFINIC HYDROCARBONS AND AROMATIC HYDROCARBONS

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This invention relates to a process for producing cyclic hydrocarbons. More specifically, the invention relates to a process for producing cycloolefins by condensing a glycol of at least 4 carbon atoms with an olefin.

An object of this invention is the condensation of an olefinic hydrocarbon with a glycol containing at least 4 carbon atoms per molecule.

Another object of this invention is the production of a cyclohexene hydrocarbon by condensing a mono-olefinic hydrocarbon with a glycol containing at least 4 carbon atoms per molecule.

A further object of this invention is the production of 1,3,5-trimethylcyclohexene by condensing 2-methylpentanediol-2,4 with propylene.

One specific embodiment of this invention relates to a process for producing a cyclo-olefin which comprises condensing an aliphatic monoolefin with a glycol having at least 4 carbon atoms per molecule at a temperature of from about 150° to about 400° C.

A further embodiment of this invention relates to a process which comprises condensing a mono-olefin with a cyclic glycol having at least 4 carbon atoms per molecule.

Cyclohexene and different alkyl cyclohexene hydrocarbons which are obtainable by the process of our invention may be hydrogenated to cyclohexane hydrocarbons, or be dehydrogenated to benzene and alkylated benzene hydrocarbons.

By the term "condensation" used in this specification and in the claims, we mean the chemical combination of a glycol of at least 4 carbon atoms with an olefin accompanied by the splitting out of water. Thus, we have found that 2-methylpentanediol-2,4 and ethylene react at 200° C. and at a superatmospheric pressure producing 1,3-dimethylcyclohexene and water as the condensation products.

Glycols utilizable in our process contain at least 4 carbon atoms per molecule and have two hydroxyl groups, these groups being preferably in the beta, gamma, and delta positions to each other. Also cyclic glycols such as 1,3- and 1,4-cyclohexanediols are utilizable in our process. Olefinic alcohols or partially dehydrated glycols such as 2-methylpentene-1-ol-4, are also useful raw materials for our condensation process.

The olefins usable in our process are preferably the normal olefins including ethylene, propylene, n-butylenes, n-pentenes, etc. Under the conditions of the reaction, some of the olefins may also undergo isomerization or polymerization accompanied by isomerization.

Our process may be carried out using either batch or continuous types of operation, although the latter is preferable. The process is carried out at a temperature of from about 150° to about 400° C., but preferably at a temperature of from about 150° to about 275° C. Superatmospheric pressures, generally of from about 10 to about 100 atmospheres, are recommended for effecting efficient operation. We prefer to employ a molar excess of the olefinic hydrocarbon relative to the glycol as this procedure tends to favor the condensation reaction.

The following example is given to illustrate the character of results obtained by the process of our invention, although the data presented are not introduced with the intention of unduly restricting the broad scope of the invention.

Ethylene, under an initial pressure of 40 atmospheres at 25° C. was introduced to a steel autoclave of 450 cc. capacity containing 58.4 grams of 2-methylpentanediol-2,4 and heated at 200° C. The product formed in this reaction was found to consist of 40 grams of normally liquid hydrocarbons and 35 cc. (approximately 22 grams) of liquefied condensible gases. About 25% of the normally liquid hydrocarbon product boiled between 124° and 135° C. and comprised essentially dimethylcyclohexene, which by hydrogenation and subsequent dehydrogenation over platinized alumina catalyst yielded meta-xylene. About 60% of the liquefied condensible gas was isobutylene.

The novelty and utility of the process of the present invention are evident from the preceding specification and example, although neither section is intended to limit unduly the broad scope of our invention.

We claim as our invention:

1. A process for producing a cyclo-olefinic hydrocarbon which comprises reacting a glycol having at least 4 carbon atoms per molecule and an olefinic hydrocarbon at a sufficient temperature and pressure that condensation of said olefinic hydrocarbon and glycol is the principal reaction of the process.

2. A process for producing a cyclo-olefinic hydrocarbon which comprises reacting a mono-olefinic hydrocarbon and a glycol having at least 4 carbon atoms per molecule at a temperature of from about 150° to about 400° C. and at a superatmospheric pressure.

3. A process for producing a cyclo-olefinic hydrocarbon which comprises reacting a mono-olefinic hydrocarbon and a glycol having at least 4 carbon atoms per molecule at a temperature

of from about 150° to about 400° C. and at a superatmospheric pressure of from about 10 to about 100 atmospheres.

4. A process for producing a cyclo-olefinic hydrocarbon which comprises reacting more than one molecular proportion of a mono-olefinic hydrocarbon and one molecular proportion of a glycol having at least 4 carbon atoms per molecule at a temperature of from about 150° to about 400° C. and at a superatmospheric pressure of from about 10 to about 100 atmospheres.

5. A process for producing a dimethylcyclohexene which comprises reacting 2-methylpentanediol-2,4 and ethylene at a temperature of from about 150° to about 400° C. and at a superatmospheric pressure.

6. A process for producing a dimethylcyclohexene which comprises reacting 2-methylpentanediol-2,4 and ethylene at a temperature of from about 150° to about 275° C. and at a pressure of from about 10 to about 100 atmospheres.

7. A process for producing a benzene hydrocarbon which comprises condensing a mono-olefinic hydrocarbon and a glycol containing at least 4 carbon atoms per molecule to produce a cyclohexene hydrocarbon, hydrogenating said cyclohexene hydrocarbon to a cyclohexane hydrocarbon, dehydrogenating the latter hydrocarbon to a benzene hydrocarbon and hydrogen, and utilizing at least a portion of said hydrogen in the hydrogenation of the cyclohexene hydrocarbon.

8. A process for producing a benzene hydrocarbon which comprises condensing a mono-olefinic hydrocarbon and a glycol containing at least 4 carbon atoms per molecule to produce a cyclohexene hydrocarbon and dehydrogenating said cyclohexene hydrocarbon to a benezene hydrocarbon.

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