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DEHYDROCYCLIZATION OF HYDROCARBONS

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This invention relates to an improved process of dehydrocyclization of hydrocarbons. More particularly, it relates to an improved process for the production of aromatic hydrocarbons for aliphatic hydrocarbons.

The art is replete with various proposals and commercial methods for the dehydrogenation of organic compounds, particularly of hydrocarbons of various types, as well as other classes of organic compounds. It is already known that the pyrolysis at high temperatures of various aliphatic hydrocarbons many times leads to the formation of more or less of aromatic hydrocarbons, the yield of aromatics usually being quite small. On the other hand, heterogeneous phase catalyses have been proposed and some are utilized commercially for the production of aromatics from aliphatic hydrocarbons. These catalysts are often provided with acidic characteristics whereby they are also effect isomerization, such as the isomerization of alkylcyclopentanes to cyclohexanes, which are then converted to aromatics. However, even these processes which are utilized on a commercial scale are subject to the usual disadvantages of heterogeneous phase catalyses, such as decrease in activity of catalyst, which necessitates, eventually, replacement or regeneration, and difficulties of providing uniform contact between the various portions of the heterogeneous catalyst and the hydrocarbon.

It is an object of this invention to provide an improved process for dehydrocyclization of hydrocarbons, and particularly for the production of aromatic compounds. A further object is to provide an improved process for the production of aromatic hydrocarbons from aliphatic hydrocarbons. A more specific object is the production of aromatic hydrocarbons from aliphatic hydrocarbons which contain a chain of at least six carbon atoms and especially from saturated aliphatic hydrocarbons. Some specific objects of the invention are to produce benzene from normal hexane, toluene from normal heptane, toluene from 2- or 3-methylhexane, and xylenes from octanes which contain a chain of at least six non-quaternary carbon atoms. A further specific object is to provide an improved process for the production of para-xylene from 2,5-dimethylhexane. It is also an object of the invention to provide an improved process for the production of fused-ring polycyclic aromatic hydrocarbons from aliphatic hydrocarbons, such as the production of naphthalene from n-decane, and from arylalkanes containing six contiguous carbon atoms, no more than two of which are in a single ring, such as the production of naphthalene from n-butylbenzene, from o-diethylbenzene, and the like.

It has now been found that cyclization of hydrocarbons containing at least six contiguous carbon atoms, no more than two of which are already in a single ring, can be effected in an efficient and improved manner by subjecting a mixture of such a hydrocarbon and a substantial proportion of free iodine to an elevated temperature sufficient to effect a C-to-H bond cleavage in the molecule in the presence of free iodine. The iodine can be supplied as free iodine or as an iodine compound which yields free iodine, either molecular or atomic, under the reaction conditions. References hereinafter to iodine are meant to include equivalent amounts of such compounds, such as alkyl iodides, e.g. ethyl iodide, propyl iodide, hexyl iodide, and the like.

Although molecular iodine generally has been regarded as unreactive toward C—H linkages, particularly in hydrocarbons, and especially in the case of saturated aliphatic hydrocarbons, it has now been found that, at elevated temperatures which are ineffective alone to effect any appreciable C-to-H or C-to-C bond cleavage in the particular hydrocarbon, heating of a substance containing at least six contiguous carbon atoms not in a single ring, for a very short time, in the presence of a substantial proportion of free iodine, effects bond cleavages and the formation of new C-to-C bonds as are necessary to provide the hydrogen deficiency for the ring formation.

For instance, when a vaporous feed mixture of n-hexane and about 1.9 mol proportions of free iodine is passed through a reaction zone at about 497° C., at atmospheric pressure and for a nominal residence time of about 37 seconds, a conversion of about 58% of the hexane results, with a yield of about 80 mol percent benzene, based on the mols of hexane converted. The hydrogen removed from the hexane is accounted for in the reaction product essentially as hydrogen iodide. In like manner, n-heptane has been converted to toluene in good conversion and yield. The other heptanes, which contain a 6-C chain, namely the 2- and 3-methylhexanes also yield toluene.

Similarly, the dimethylhexanes, namely, 2,3-, 2,4-, 3,4- and 2,5-dimethylhexanes, which can yield only one dimethylbenzene (one xylene) for a given dimethylhexane, by dehydrocyclization in the absence of isomerization, yield the corresponding xylenes. For instance, when a vaporous feed mixture of 82% 2,5-dimethylhexane and 18% 2,5-dimethylhexene -3 and about 2.4 mol proportions of free iodine was passed through an unobstructed reaction zone (empty quartz tube: 4 cm. inside diameter, 811 cc. volume) at about 500° C., at atmospheric pressure and for a nominal residence time of about 5 second, a conversion of about 63% of the 2,5-dimethylhexane was obtained, with a yield of about 97% aromatics, being about 96% C_8-aromatics which was about 99% para-xylene. This fraction was essentially free from the isomers, ortho- and meta-xylene, indicating the avoidance of any significant amount of isomerization. Furthermore, the amount of degradation was only very small, as indicated by a yield of only about 0.9% of toluene, representing only a monodemethylation, and only about 0.1% benzene, representing di-demethylation. Similarly, 2,4-dimethylhexane yields essentially only meta-xylene, and 2,3-dimethylhexane and 3,4-dimethylhexane yield essentially only ortho-xylene in the xylene fraction.

As higher homologues are reacted in accordance with this invention, the possibilities for the production of a plurality of individual aromatic compounds from a single

molecular species increase, and usually a mixture of several aromatics is obtained from a given substance. Thus, it has been found that normal decane yields a large proportion of substituted benzene compounds and even a portion of naphthalene. Among the benzene compounds which are obtained are toluene, ethylbenzene, ortho-methylpropylbenzene, butylbenzene, ortho-diethylbenzene, propylbenzene and beta-methylstyrene; some degration by way of demethylation occurs. It will be noted that a styrene was produced, namely, beta-methylstyrene, possibly by the dehydrogenation of n-propylbenzene.

When normal octane, which by aromatization without demethylation and in the absence of isomerization can yield only ortho-xylene or a C_2-alkylbenzene (or C_2-alkenylbenzene), is subjected to similar conditions in the presence of a substantially chemical equivalent of free iodine, the C_8-product aromatic fraction is made up of ortho-xylene, ethylbenzene and styrene. When the temperature of the process or I_2 or total conversion is raised, the ratio of styrene to ethylbenzene increases. When ethylbenzene is subjected to similar conditions admixed with about 0.6 mole of iodine per mole of ethylbenzene, a yield of about 90% styrene, based on the ethylbenzene converted, is obtained.

The dehydrocyclization of 3-methylheptane by reacting in the vapor phase with free iodine at a temperature of about 500° C. yields, as C_8-aromatic product, a mixture of ethylbenzene, styrene and ortho- and paraxylenes. When the temperature of reaction, or I_2 fed or conversion, is raised, the proportion of styrene in the product is substantially increased.

Of course, as is readily understood, certain higher homologues can give only a single aromatic by the dehydrocyclization, without degradation or isomerization. Thus, 2,3,4,5-tetramethylhexane yields only prehnitene; 2,3,5-trimethylheptane yields three benzene derivatives, namely, durene, 3,4-dimethylethylbenzene and 3,4-dimethylstyrene.

In addition to the dehydrocyclization of cyclic hydrocarbons, as shown by the preceding representative instances, dehydrocyclization can be effected with substances which contain cyclic structures and which contain six contiguous carbon atoms which are not already in a single ring. Thus, arylalkanes and arylalkenes which contain six contiguous carbon atoms, including no more than two atoms of a single aromatic ring, such as n-butylbenzene, o-diethylbenzene, o-methylpropylbenzene, and the like, may be dehydrocyclized by the present invention to give corresponding compounds containing an additional ring, such as naphthalene, and the like. Similarly, alpha-ethylnaphthalene upon dehydrocyclization gives acenaphthene and acenaphthylene; 1,2-diethylnaphthalene gives phenanthrene; and o-methylbenzene gives anthracene and dihydroanthracene.

As disclosed and claimed in copending application Serial No. 489,303 of applicant and Richard D. Mullineaux, a carbon atom of a chain of at least two carbon atoms attached directly to a quaternary carbon atom undergoes a cleavage from the quaternary C-atom and forms a new C-to-C linkage with another C-atom attached directly to the quaternary C-atom, thereby changing the quaternary C-atom to a non-quaternary C-atom and lengthening the chain of contiguous C-atoms. Thus, 2,2,5-trimethylhexane is isomerized to a 2,6-dimethylheptane structure, with dehydrodemethylaromatization to m-xylene, in addition to the conversion indicated just before.

As already described generally, the conditions for carrying out the process of this invention are selected such that, in the absence of the iodine there would be only a relatively low rate and amount of dehydrocyclization. This, of course, depends on the particular compound being converted. For the dehydrocyclization of hydrocarbons, the temperature required is at least about 300° C., generally being at least about 350° C., and usually preferably in the order of about 425°–525° C. Although, higher temperatures may be utilized up to about 600° C., but it is usually preferred not to go above about 575° C. Higher temperatures are not objectionable so long as other undesirable changes are not effected. However, excessively high temperatures are not required in order to effect suitabl dehydrocyclization in the presence of the relatively large proportion of iodine.

In the case of less thermally stable substances, the temperature is more suitably adjusted within the lower range of values, such as about 400° C. to 450° C., and in some cases it may be as low as about 300° C. to 350° C. Thus, lower temperatures effect less dealkylation, which tends to be greater the more highly branched the hydrocarbon starting material, as well as the longer the hydrocarbon chain.

An important factor in the practice of the invention is the carrying out of the conversion in the presence of a substantial proportion of free iodine. Advantageous results are obtained by the use of an amount of iodine which is of the order of the chemical equivalent of the dehydrogenation to be effected. A smaller proportion may be utilized for lower conversions and yields under otherwise similar reaction conditions. In order to obtain the maximum conversion of the substance to the desired dehydrocyclized product, two atomic proportions of iodine are required per new C-to-C linkage. For example, in the case of n-hexane being converted to benzene, there is the cleavage of eight C-to-H linkages and the formation of four new C-to-C linkages, thus requiring eight atomic or four molecular proportions of iodine. As a practical matter about one-half this amount gives good results, although there is only partial conversion. The unreacted material is recoverable and can be recycled to react with a further (or regenerated) portion of iodine. Of course, an excess of free iodine can be used to insure a sufficient concentration of iodine in the vapor phase when the concentration of n-hexane has been reduced to a low value. As a practical matter, however, something less than complete conversion in a single stage represents a more realistic operation. So that even in such cases as for n-hexane, about 90% of the theoretically chemical equivalent of iodine (mole ratio of I_2/hydrocarbon=3.6) is a preferred upper limit on the proportion of iodine. On the other hand, in order for the process to have practical utility, it is required that at least about 5% of the initial hydrocarbon reactant be converted in a single pass to the desired dehydrogenation product, so that the proportion of iodine is such that twice the moles of iodine is at least 5% of the product of the number of moles of hydrocarbon and the number of hydrogen atoms to be removed per molecule to yield the aromatic hydrocarbon. Particularly suitable mole ratios of I_2/hydrocarbon are from about 0.6 to about 4, although still higher ratios can be used, such as 6–8, the higher ratios being preferable when the hydrocarbon represents four or more equivalents in the dehydrogenation.

The process is suitably carried out at various pressures, from subatmospheric to superatmospheric pressures in vapor phase. Although atmospheric pressure is suitable and is advantageous in most cases, other considerations, such as factors which are involved in the separation and recovery of the hydrogen iodide from the product stream, in some cases make a superatmospheric pressure more desirable. Thus the pressure can be at any value at which the reactants are sufficiently vaporized at a temperature at which the hydrocarbon is substantially thermally stable. The pressure can be, for example, as high as from 500 to 1000 pounds per square inch, and even higher in some cases.

The influence of the proportion of iodine on the conversion of n-hexane can be seen from the data in Table I, which gives details of reaction conditions and of product analyses.

Table I.—Reaction of n-hexane and iodine

Pressure: 1 atmosphere
Temperature: 497°-527° C.
Reactor: Quartz tube (4 cm. I.D.; 811 cc.)
n-Hexane Fed: 1 mol
Nominal Residence Time [a]: 0.5-0.8 minute

I_2/n-Hexane (molar)	<0.01	0.111	[b] 0.25	0.62	1.86
Temperature, ° C	527	527	527	527	497
Reacted:					
n-Hexane (percent)	20	39.6	≤53	49.5	57.7
I_2 (percent)	100	99	~100	98	96
	Equivalents (percent of Reacted)				
Produced:					
Benzene	<1	16	30	46	80
Dienes+Cyclohexene		1		1	
Hexenes (C_6H_{12})	1	12		5	8
Total C_6's	≤2	29	>30	52	88
Total C_1-C_5	98	70	[c]	48	7
Hydrogen [d]	4	3	6	14	9
Hydrogen Iodide	~100	93.5		94	99.2
Total C_2-C_5 sats/Total C_2-C_5 olefins	0.36	1.8		5.6	7

[a] Computed from total molar input rate at reaction T.
[b] Fed as C_2H_5I (0.50 mol).
[c] Not obtainable because of products from C_2H_5I.
[d] Mols/100 mols hexane reacted.

The influence of temperature on the process will be seen from the data in Table II, for the reaction of n-hexane and iodine.

Table II.—Reaction of n-hexane and I_2: Effect of temperature

Pressure: 1 atmosphere
Reactor: Quartz tube (4 cm. I.D.; 811 cc.)
Nominal Residence Time: ca. 0.5 minute
I_2/C_6H_{14} (molar): 0.4

Temperature, ° C	527	497
$C_6H_6/(C_1-C_5)$ (molar)	0.60	0.75

Thus, as seen from the data of Table I, as the I_2/C_6H_{14} mol ratio is raised from <0.01 to 0.6 at a constant temperature of 527° C., and a roughly constant contact time, not only does the rate of hexane disappearance rise, but the nature of the products changes profoundly. Whereas in the absence of iodine the reaction is principally degradation to smaller molecules through consecutive scission of free radicals, the addition of iodine rapidly enhances the preservation of the C_6 structure. The use of iodine in increasing proportions not only reduces the amount of C_1—C_5 products but markedly increases the saturate to olefin mol ratio of these lighter products.

According to the data in Table II, reduction of the operating temperature from 527° C. to 497° C. at constant I_2/C_6H_{14} mol ratio in the feed also enhances retention of the C_6 structure. When both reduced temperature and high I_2/C_6H_{14} mol ratio are employed, an unusually high C_6-structure yield is obstained and the overall reaction closely approaches the stoichiometry:

$$n\text{—}C_6H_{14}+4I_2 \rightarrow C_6H_6+8HI$$

Since, as is well known, hydrogen iodide may be decomposed to produce free hydrogen and iodine, catalyzed or uncatalyzed, or may be reacted with an oxidizing agent, such as oxygen, to form free I_2, the iodine can be readily regenerated and recycled to the rehydrogenation zone for further utility in the process.

It is to be seen from the data in Table I that essentially all of the iodine was converted to hydrogen iodide. Thus, this essentially complete absence of iodine does not correspond to the equilibrium concentration of free iodine for the reaction: $2HI=H_2+I_2$, at the reaction zone temperature. Therefore, it is advantageous to carry out the reaction, at least the later stage(s) thereof, in the presence of a catalyst for the decomposition of hydrogen iodide into hydrogen and iodine. It is thereby feasible to increase the concentration of free iodine in the system above that which prevails downstream in the reaction zone in the absence of a catalyst for hydrogen iodide decomposition, and without further addition of free iodine into the reaction zone at that point. It is also contemplated, however, to increase the concentration of free iodine by such addition from an extraneous source.

It is also an aspect of the present invention to supply to the reaction zone, preferably at one or more points on the downstream side of the entrance thereto, an oxidant for hydrogen iodide to combine with the hydrogen thereof and give free iodine. For this purpose different substances may be utilized, usually in less than stoichiometric proportions, such as oxygen (in air), nitrogen dioxide, sulfur, etc. For this purpose, the amount of oxidizing agent will usually be from about 0.1 to about 0.9 chemical equivalent of the total iodine (all forms) present. Thus, when using free oxygen, either as such or in a mixture with an inert gas, such as nitrogen, as in air, or carbon dioxide, etc., 8 parts by weight of oxygen is the chemical equivalent of 127 parts by weight of iodine, so that the oxygen used is generally from about 0.5% to 5% by weight of the iodine (counting it as iodine in both free form and as iodide). When the iodine is proposed to be recovered from any resulting hydrogen iodide by oxidation, there is no disadvantage to the recovery in effecting the oxidation in the reaction zone. In that case, a chemical equivalent of the oxidizing agent can be utilized. However, when it is desired to recover the hydrogen, which is removed from the hydrocarbon, as free hydrogen, as by pyrolysis of the hydrogen iodide to hydrogen and iodine, it is desirable to use the minimum amount of oxidizing agent in the reaction zone which is sufficient for the desired conversion and yield.

The products of the reaction are readily separated for the recovery of the aromatic hydrocarbon, separation of the unreacted hydrocarbon reactant for recycling, and separation of the hydrogen iodide and its reconversion to free iodine for recycling. Free iodine in the product stream can be separated with the hydrocarbons and then separated from them by a subsequent operation.

The discovery that hydrocarbons having chains of at least six nonquaternary C-atoms can be readily converted to aromatics by vapor phase reaction in the presence of a substantial reactive proportion of free iodine can be utilized for the large scale production of aromatics. Furthermore, the process can be applied to a mixture of such non-aromatic hydrocarbons. The resulting mixture of aromatic and unchanged non-aromatic hydrocarbons, which may have overlapping boiling points, can then be separated as by a solvent extraction or an extractive distillation utilizing a selective solvent for the aromatics.

I claim as my invention:

1. A process for the production of aromatics by dehydrocyclization of a hydrocarbon containing at least six contiguous non-quaternary carbon atoms in a chain, no more than two of which are in a single ring, which comprises injecting said hydrocarbon into a reaction zone, heating it therein in the presence of at least about 0.6 mole of free iodine per mole of said hydrocarbon in vapor phase for a time not exceeding about 0.8 minute at a temperature of at least 300° C. to effect C-to-H bond cleavages in the molecule in the presence of free iodine, whereby said iodine is converted to hydrogen iodide and at least about 46 mole percent of the hydrocarbon converted is dehydrocyclized to an aromatic product, withdrawing the resulting reaction mixture from said reaction zone and recovering said aromatic product from said mixture.

2. A process in accordance with claim 1, wherein the hydrocarbon is an acyclic aliphatic hydrocarbon.

3. A process in accordance with claim 1, wherein the hydrocarbon is an aryl-substituted aliphatic hydrocarbon.

4. A process in accordance with claim 1, wherein the mol ratio of iodine to hydrocarbon is from about 0.6 to about 8.

5. A process in accordance with claim 1, wherein the hydrocarbon has a chain of six carbon atoms having only

hydrogen and methyl substituents on said six carbon atoms.

6. A process in accordance with claim 5, wherein the hydrocarbon contains only eight carbon atoms.

7. A process in accordance with claim 1, wherein the hydrocarbon is an *x*,*y*-dimethylhexane in which *x* and *y* refer to different carbon atom positions from 2 to 5, inclusive, in the hexane chain.

8. A process in accordance with claim 1, wherein the hydrocarbon is 2,5-dimethylhexane and the recovered dehydrocyclized product is p-xylene.

9. A process in accordance with claim 1, wherein the hydrocarbon is n-hexane and the recovered dehydrocyclized product is benzene.

10. A process in accordance with claim 1, wherein the hydrocarbon is a heptane and the recovered dehydrocyclized product is toluene.

11. A process according to claim 10, wherein the hydrocarbon is n-heptane.

12. A process in accordance with claim 1 wherein said hydrocarbon is a saturated hydrocarbon.

13. A process in accordance with claim 1 wherein said hydrocarbon is an olefin.

14. A process in accordance with claim 1 wherein substantially the entire charge to the process consists of saturated hydrocarbons containing at least six contiguous non-quaternary carbon atoms in a chain, no more than two of which are in a single ring.

15. A process in accordance with claim 1 wherein substantially the entire charge to the process consists of olefinic hydrocarbons containing at least six contiguous non-quaternary carbon atoms in a chain, no more than two of which are in a single ring.

16. A process according to claim 1, in which said resulting reaction mixture is cooled prior to recovering said dehydrocyclized product of the hydrocarbon.

References Cited in the file of this patent

UNITED STATES PATENTS

1,925,421	Van Peski	Sept. 5, 1933
2,259,195	Baehr et al.	Oct. 14, 1941
2,315,499	Cantzler et al.	Apr. 6, 1943
2,492,844	Condon	Dec. 27, 1949
2,666,798	Condon	Jan. 19, 1954

FOREIGN PATENTS

849,804	France	Aug. 28, 1939

OTHER REFERENCES

Chemical Abstracts, vol. 25 (1931), page 5967[9].

Bairstow et al.: "Jour. Chem. Soc." (1933) page 1158.

Hydrocarbons from Petroleum, Rossini et al., Reinhold Publishing Corp., N.Y. (1953), pages 407–409.