Patented Apr. 22, 1952

2,593,446

UNITED STATES PATENT OFFICE

2,593,446

PRODUCTION OF CYCLIC MONOOLEFINS

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No Drawing. Application September 3, 1949, Serial No. 114,067

18 Claims. (Cl. 260—666)

1

The present invention relates to the selective dehydrogenation of hydrocarbons and is more particularly concerned with the production of cyclohexene and/or its isomer methylcyclopentene from relatively cheap raw materials such as petroleum hydrocarbon fractions rich in methylcyclopentane.

Many crude petroleum hydrocarbon oils and hydrocarbon oil fractions derived from other sources of appropriate boiling range are rich in methylcyclopentane (MCP) and can therefore be employed as a starting material in accordance with the present invention. Methylcyclopentane, by the loss of 2 atoms of hydrogen is converted to methylcyclopentene which can be isomerized to cyclohexene, or under some conditions such isomerization may take place simultaneously with dehydrogenation.

In attempting to dehydrogenate methylcyclopentane, however, over the usual dehydrogenation catalysts, only comparatively low yields of monoolefins are obtained with an accompanying high production of hydrocarbonaceous deposit known as "coke." By the addition of hydrogen to the feed charged to the dehydrogenation process some increase in monoolefin yields can often be obtained, which may also be accompanied by some reduction in coke make.

I have now found that by the presence of small amounts of an aromatic hydrocarbon, preferably benzene, during the initial stages of catalytic dehydrogenation of methylcyclopentane or of a C_6 hydrocarbon fraction rich in methylcyclopentane, and particularly in the further presence of certain quantities of hydrogen added to the charge, improved yields of monoolefins are obtained with the production of considerably reduced quantities of coke.

In carrying out the catalytic dehydrogenation of the methylcyclopentane fraction in accordance with the present invention, a product containing monoolefins is obtained comprising methylcyclopentene and including, depending on conditios, greater or less quantities of cyclohexene. From this product cyclohexene concentrates may be obtained by isomerization of the methylcyclopentene in known manner with or without previous separation of the methylcyclopentene from the dehydrogenation product. Cyclohexene is a valuable starting material for use in organic synthesis since it is readily oxidized to adipic acid, useful in the production of ester plasticizers and important as an intermediate for the production of long chain synthetic linear polyamides, such as nylon. It is, however, unnecessary to separate cyclohexene from accompanying hydrocarbons in the dehydrogenated product, since the entire product or an easily separated fraction thereof containing cyclohexene can be subjected to oxidation with subsequent separation from the

2

oxidation product of the adipic acid thus formed.

Although in the process of dehydrogenating methylcyclopentane and/or cyclohexane greater or less quantities of benzene are formed as by-product in previously known processes, such formation of benzene in the process does not satisfy the requirement of the invention that benzene be present during the initial stages of the reaction; since, it has been found, that only under conditions that the benzene is initially present does it exert any significant influence on yields of monoolefins or on reducing coke formation. As starting material for use in the present invention, methylcyclopentane is preferred to cyclohexane, since the latter material has a greater propensity to favor dehydrogenation to benzene rather than to cyclohexene.

The crude dehydrogenation product will generally contain in addition to unreacted methylcyclopentane with or without some cyclohexane, various quantities of methylcyclopentene-1, methylcyclopentene-2, cyclohexene, C-6 dienes and benzene. Because of the relatively close boiling points of these compounds, separation of products by ordinary distillation methods is relatively difficult. If desired, however, separation can be effected by extractive distillation with selected agents such as phenols, cresylic acid, nitrobenzene, furfural, or the like; or by azeotropic distillation which will yield a fraction containing the monoolefins together with benzene separated from the saturated residue.

Other aromatic hydrocarbons that may be employed instead of benzene with some improvement in monoolefin yields and/or reduction of coke make over processes employing no added aromatic hydrocarbons, include toluene, naphthalene and methyl-naphthalene, particularly α-methyl naphthalene. It is not to be understood, however, that these polynuclear aromatic compounds or methyl substituted mono- or polynuclear compounds necessarily obtain the same improved results as the preferred benzene. The use of naphthalene introduces increased separation problems. The methyl substituted compounds, while apparently having the tendency to improve monoolefin yields to almost the same extent as in the case of benzene and while also effecting some decrease in coke deposit over processes employing no aromatic hydrocarbon additive, also have a tendency to become demethylated under the conditions of the reaction, increasing the quantity of low molecular weight gas produced. Benzene, moreover, being one of the products of reaction, can be easily recycled to the dehydrogenation step, avoiding the necessity and expense of procuring the same from outside sources, once the process has been started up.

The dehydrogenation of the methylcyclopen-

tane fraction may be carried out under pressure conditions such that the partial pressure of the methylcyclopentane is at atmospheric pressure or below, for instance the total pressure being at atmospheric, employing any of the usual dehydrogenation catalysts, preferably composites of alumina with chromia, molybdena, etc., and at temperatures in the order of about 850–1100° F. Present indications are that best results are obtained with chromia-alumina catalyst in the temperature range of about 900–1100° F. and in the presence of about 2–5 mols of hydrogen per mol of methylcyclopentane charged. Since the process results in a net production of hydrogen, the hydrogen-containing gas formed in the process may be separated and recycled to the dehydrogenation step. The benzene may be added to the charge in required amount, or the catalyst may be prewetted with the benzene, or the thus prewetted catalyst may be employed with further addition of benzene to the charge; however, not with equal results as will hereinafter appear. In the addition of benzene to the charge only very small amounts are necessary, for example not in excess of 4% benzene; optimum yields of monoolefins with low coke production and comparatively high ratios of monoolefins to coke are obtained by the use of about 0.5 to 2% benzene by weight of methylcyclopentane charged. Larger amounts of benzene as up to about 5 to 10% result in coke production of 20–30% higher than the optimum range, while still larger quantities of added benzene, although further increasing the yield of monoolefins somewhat, do so only at the expense of disproportionately increased coke production. The same conditions and proportions also apply in the case of the suggested substitutes for benzene.

The isomerization of methylcyclopentene to cyclohexene may be carried out under known catalytic olefinic isomerizing conditions, for example employing natural or synthetic solid adsorbtive aluminous materials as catalyst, such as activated alumina or bauxite, and particularly those materials which contain large quantities of gamma alumina. Temperatures of about 200–600° C. may be employed at atmospheric pressure or somewhat above. Other olefin isomerization catalysts that may be employed include acid activated clays and synthetic silica-alumina composites which may contain small amounts of other oxides such as those of beryllium, thorium, zirconium, etc.

EXAMPLE I

To a mixture of 99% by weight substantially pure methylcyclopentane (99.5% pure) and 1% by weight of benzene there was added 3.5 mols of hydrogen per mol of oil, and the charge passed over a stationary bed of chromic oxide-alumina catalyst (20% Cr_2O_3, 80% Al_2O_3 by weight). The catalyst previous to use had been treated for one hour at 900° F. in a hydrogen stream. The hydrocarbon charge including the hydrogen was passed over the catalyst at a ratio of catalyst to oil of 2:1 for thirty minutes or at a liquid space velocity of 1 volume of oil per volume of catalyst per hour, at a temperature of 1050° F. and at atmospheric pressure. The effluent from the reactor was cooled in a condenser, through the jacket of which a brine solution was circulated at 0 to 5° C. The condensed materials were received in an ice cooled vessel while the vapors were passed through a second condenser immersed in an acetone-Dry Ice bath connected to a second receiver communicating with a gas collector.

The yields obtained are shown in the following table:

Table 1

PRODUCT DISTRIBUTION WEIGHT PERCENT OF METHYLCYCLOPENTANE CHARGE

Monoolefin	Diolefin	Benzene	Gas	Coke	Conversion
12.2	2.3	10.4	1.8	3.0	29.7

Repetition of the experiment under identical conditions but employing 99.5% of the methylcyclopentane and 0.5% of added benzene by weight, resulted in the yield of 11.5% monolefins (per weight of methylcyclopentane charged) and 2.6% by weight of coke. With less than 0.5% of benzene added, no significant reduction in coke occurred; thus with 0.2% added benzene there was obtained 5.8% coke as compared with 6.5% by weight of coke without benzene addition.

Various amounts of benzene added to the charge as between about 0.5% and 2.0% in another series of runs under the same conditions resulted in a product distribution which did not differ markedly from that obtained employing 1.0% benzene, and falling in a range of about 11.5 to about 12% monoolefins with the production of from about 2% to less than 3% coke.

The effect of changes in operating conditions and of the effect of addition of hydrogen and benzene to the charge will be seen from the following table showing the yields obtained under the various conditions tabulated, employing the same chromic oxide-alumina catalyst as in the previous example at a catalyst/oil ratio of 2:1.

Table 2

Reaction Conditions			Charge			Product Distribution, Weight Percent of MCP Charge					
Temp., °F.	Liq. S. V. v./v./Hr.	Press. mm. Hg	H_2: oil mole ratio	Benzene, Weight Percent	MCP, Weight Percent	Monoolefin	Diolefin	Benzene	Gas	Coke	Conversion
1,050	1.0	74	0	0	100	6.4	1.7	4.3	5.0	12.5	29.9
1,050	1.0	(1)	3	0	100	9.6	1.4	5.2	1.8	11.3	29.3
1,050	1.0	12	0	10	90	3.8	2.4	7.8	5.7	8.3	28.0
1,050	1.0	(1)	1.5	10	90	12.9	2.6	7.9	3.6	6.5	33.5
1,050	2.0	(1)	3	10	90	9.4	3.1	8.1	2.6	4.1	27.3
1,050	1.0	(1)	3	10	90	14.1	3.1	6.6	4.9	3.6	32.3
900	1.0	(1)	3	10	90	8.1	1.0	6.0	1.8	0.3	17.2
950	1.0	760	0	0	100	5.4	1.0	6.9	4.7	7.2	25.2
950	1.0	(1)	3	10	90	10.4	1.7	6.2	2.0	0.6	20.9
1,150	3.0	10	0	0	100	3.7	1.3	9.5	2.6	5.4	22.7
1,150	1.0	(1)	3	0	100	16.9	.1	12.1	2.2	17.4	48.7
1,150	1.0	(1)	3	10	90	14.1	3.1	10.4	4.6	7.1	39.3
1,050	1.0	(1)	3	100	----------	.6	0	--------	0.4	0.2	1.2

[1] Total pressure: atmospheric.

It will be seen from the foregoing that by the use of benzene and hydrogen added to the methylcyclopentane charged to the process, coke deposition is appreciably lower and that the full effect of such reduction is obtained only when both hydrogen and benzene are employed. Not only is the quantity of coke thus reduced, but the conversion to desirable products including monoolefins is thereby also considerably enhanced. This effect of adding benzene to the charge is all the more surprising when considering that benzene is a product of reaction necessarily produced in the process. It also appears from the tabulation above that products obtainable from benzene and hydrogen, as such, do not account for their behavior in the process, since under the run conditions employing these materials alone, only minute quantities of coke and monoolefins are obtained.

Another series of runs were carried out with variations in the molar ratio of hydrogen to oil, under otherwise identical conditions. It was found that reduction in hydrogen to molar ratios below about 1:1 at constant space velocity resulted in a marked increase in coke formation, but otherwise had little effect on product distribution except at very high hydrogen to oil ratios in excess of about 5:1, at which high ratios considerable reduction of the monoolefin yield takes place.

EXAMPLE II

A charge consisting of 90% substantially pure methylcyclopentane and 10% α-methylnaphthalene was dehydrogenated over the same chromic oxide-alumina catalyst as in the previous example, with 3 mols of hydrogen per mol of hydrocarbon being added to the charge. The operation was carried out at a liquid space velocity of 1 volume of oil per volume of catalyst per hour and at a catalyst to oil weight ratio of 2, at a temperature of 1050° F. and atmospheric pressure. The yields are given in the following tabulation:

PRODUCT DISTRIBUTION—WEIGHT PERCENT MCP CHARGED

Monoolefin	Diolefin	Benzene	Gas	Coke	Conversion
13.8	6.2	2.4	7.5	5.4	31.4

The gas contained a large percentage of methane apparently as a result of dealkylation of the α-methylnaphthalene.

EXAMPLE III

The effect of prewetting the catalyst with benzene instead of adding the benzene to the charge will be seen from the operation described below:

In these runs the same chromic oxide-alumina catalyst as was employed in the previous examples was wetted with 5 cc. benzene per 100 cc. of catalyst (approximately 2% benzene by weight of methylcyclopentane to be charged) by passing vaporized benzene over the hot catalyst prior to beginning the run. The runs were made under the following conditions:

Temperature—1050° F.
Liquid space velocity—1 vol./vol./hr.
Catalyst/oil weight ratio—2:1
Hydrogen to oil mol ratio—3:1

with the results tabulated below:

An additional series of runs were made using the catalyst prewetted with benzene as before, but with the further addition of a small amount of

benzene to the charge (98% MCP–2% benzene); the results being also tabulated below:

Table 3

PRODUCT DISTRIBUTION—WEIGHT PERCENT MCP CHARGED

Percent added Benzene in charge	Monoolefin	Diolefin	Benzene	Gas	Coke	Conversion
0	16.9	3.9	13.7	3.6	5.1	43.2
0	16.4	2.2	12.6	3.0	4.4	38.6
0	16.4	4.4	9.4	3.3	5.1	38.6
2	12.3	2.5	6.3	6.4	2.8	30.3
2	12.1	3.2	6.2	5.9	3.1	35.0
2	13.7	2.4	4.5	5.3	2.9	28.8

In the last run of the above tabulation the catalyst was purged with hydrogen for ten minutes after prewetting with benzene and before starting the run.

In general, it appears that at temperatures of 900–1100° F., liquid space rates up to about 5 and preferably from about 1 to 3 volumes of oil per volume of catalyst per hour should be employed in the dehydrogenation of methylcyclopentane, while catalyst to oil ratios are also best maintained below 5:1 and at about 1:1 to 3:1 for optimum over-all results.

Regeneration of the catalyst may be carried out in known manner by contact with air or other oxygen-containing gas at temperatures of about 900–1100° F. to effect combustion of the coke. In employing a fixed catalyst bed, the regeneration step is alternated in timed sequence with the on-stream dehydrogenation step, while in moving bed processes the dehydrogenation and regeneration steps are carried out in separate vessels, the catalyst being moved continuously in cycle between the vessels.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim as my invention:

1. In the dehydrogenation of methylcyclopentane in contact with dehydrogenation catalyst for production of high yields of monoolefins, the improvement which comprises reducing coke formation during the process by effecting the dehydrogenation in the presence of about 0.5 to 4% of an added aromatic hydrocarbon by weight of said methylcyclopentane, said added amount of aromatic hydrocarbons being present exclusive of any aromatic hydrocarbons formed in the process.

2. The process in accordance with claim 1 wherein the dehydrogenation of said methylcyclopentane is carried out in the further presence of about 1 to 5 mols of hydrogen per mol of methylcyclopentane.

3. The process in accordance with claim 2 wherein said aromatic hydrocarbon consists of benzene.

4. The process in accordance with claim 1 wherein said aromatic hydrocarbon consists of benzene.

5. The process in accordance with claim 1 wherein the dehydrogenation is carried out in the presence of not more than 2% of said aromatic hydrocarbon by weight of said added methylcyclopentane, said aromatic hydrocarbons being selected from the group consisting of benzene and naphthalene and monomethyl derivatives of these.

6. The method of producing monoolefins from hydrocarbon fractions rich in methylcyclopentane which comprises subjecting such a fraction in admixture with at least equi-molar quantities of hydrogen to dehydrogenation conditions in contact with a dehydrogenation catalyst in the presence of 0.5 to 4% benzene by weight of the methylcyclopentane in said fraction.

7. The method in accordance with claim 6 wherein 0.5 to 2% by weight of benzene are included in the hydrocarbon fraction charged.

8. The method in accordance with claim 6 wherein the catalyst is pretreated with benzene.

9. The method in accordance with claim 6 wherein said catalyst comprises chromic oxide-alumina which has been pretreated with hydrogen.

10. The method in accordance with claim 6 wherein said catalyst comprises chromium oxide-alumina which has been pretreated with benzene and thereafter with hydrogen.

11. In the production of cyclohexene from a hydrocarbon fraction rich in methylcyclopentane the improvement which comprises contacting such a fraction containing added hydrogen with an alumina-containing dehydrogenation catalyst in the presence of 0.5 to 10% benzene added, at a temperature in the range of 900–1100° F., at a partial pressure of methylcyclopentane not in excess of atmospheric, employing a ratio of catalyst to oil of 1:1 to 5:1 and at a liquid hourly space rate of between 1 and 5 volumes of oil per volume of catalyst per hour.

12. The method in accordance with claim 11 wherein said catalyst consists essentially of chromium oxide and alumina.

13. The method in accordance with claim 11 wherein said catalyst consists essentially of chromium oxide and alumina which catalyst has been pretreated with hydrogen.

14. The method in accordance with claim 11 wherein said catalyst has been prewetted by passing benzene vapors thereover previous to contacting the hydrocarbon charge therewith.

15. The method in accordance with claim 11 wherein said catalyst prior to contact of the hydrocarbon charge therewith is pretreated with benzene vapors and with hydrogen.

16. The method of producing monoolefins by dehydrogenation of methylcyclopentane which comprises subjecting a charge comprising a mixture of methylcyclopentane and hydrogen to contact with a chromic oxide-alumina catalyst under dehydrogenation conditions, said charge including 0.5 to 2% benzene by weight of methylcyclopentane in the charge.

17. The method of producing monoolefins by dehydrogenation of methylcyclopentane which comprises subjecting a charge comprising a mixture of methylcyclopentane and hydrogen to contact with a chromic oxide-alumina catalyst under dehydrogenation conditions, said catalyst containing not less than 0.5% benzene adsorbed thereon as a result of pretreatment with benzene vapor prior to initial contact of the charge therewith.

18. A method for the production of C_6 monoolefins by the catalytic dehydrogenation of methylcyclopentane which comprises passing a mixture comprising methylcyclopentane and hydrogen in the molar ratio of 2 to 5 mols of hydrogen per mol of methylcyclopentane into contact with a composited catalyst consisting essentially of a major portion of alumina and a minor portion of chromic oxide, at a temperature within the range of about 900 to 1100° F., at a liquid hourly space rate of between 1 and 3 volumes of methylcyclopentane per volume of catalyst per hour employing a ratio of catalyst to methyl cyclopentane between 1:1 and 3:1, the contact of said mixture with said catalyst being effected in the presence of 0.5 to 2% benzene by weight of methylcyclopentane charged.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,385,555	Voge	Sept. 25, 1945
2,412,936	Heppe	Dec. 17, 1946

OTHER REFERENCES

Oblad et al.: "Jour. Am. Chem. Soc.," vol. 62 (1940), pages 2066–2069.

Herington et al.: "Proceeding Roy. Soc. London," vol. 190 (1947), pages 289–308.