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3,349,140

### USING RUTHENIUM CATALYSTS TO PREPARE CIS-ISOMERS OF POLYCYCLIC AROMATICS

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9 Claims. (Cl. 260—667)

This is a continuation-in-part of copending application U.S. Serial No. 372,692, filed June 4, 1964 now abandoned.

This invention relates to the preparation of cis-isomers of hydrogenated aromatic hydrocarbons and more particularly to the preparation of increased amounts of saturated cis-isomers of bicyclic and tricyclic aromatic hydrocarbons. These cis-isomers are defined with respect to the common carbon atoms of the cyclic hydrocarbons and, in the case of the mono-methyl cis-isomers, include both the cis-syn and cis-anti isomers. The cis-isomers have the general characteristic of high heats of combustion and higher densities, and therefore are highly desirable as high-energy components of jet fuel.

Illustrative of the above-described properties of the cis-isomers, the cis-isomers of 2-methyldecalins have heats of combustion of about 1200 to about 3400 cal./mole greater than the heats of combustion of the trans-isomers of 2-methyldecalins. In addition, the cis-syn-2-methyldecalin has a density of 0.8812 gms./ml. at 20° C. while trans-syn-2-methyldecalin has a density of 0.8568 gms./ml. at 20° C. Table I, shown below, indicates the relative properties of these and other various isomers of decalin, 1-methyldecalin and 2-methyldecalin, as desirable products from the inventive process. In Table I,  $\Delta H$  indicates the calculated differential in the heat of combustion for each isomer in a series, relative to the member in the series having the lowest heat of combustion.

TABLE I

Compound	$\Delta H$ (Heat of Combustion), Cal./Mole	Density, $d^{20}$
Cis-syn-1-methyldecalin.....	2,500	.8926
Cis-anti-1-methyldecalin.....	2,800	.885
Trans-syn-1-methyldecalin.....	1,700	.8834
Trans-anti-1-methyldecalin.....	0	.8868
Cis-syn-2-methyldecalin.....	3,400	.8812
Cis-anti-2-methyldecalin.....	3,400	.8771
Trans-syn-2-methyldecalin.....	0	.8568
Trans-anti-2-methyldecalin.....	2,200	.871
Cis-decalin.....	2,100	.8963
Trans-decalin.....	0	.8699

Although the cis-isomers are preferred, they are thermodynamically less favored than the trans-isomers. It is therefore desirable to have a process in which the thermodynamics are avoided and increased amounts of the cis-isomers are produced.

It has been found unexpectedly that cis-isomers of hydrogenated polycyclic aromatic hydrocarbons having 2-3 fused cyclic units are produced in an amount which is substantially greater than the amount which is present at equilibrium when the bicyclic and tricyclic aromatic hydrocarbons are contacted with a catalyst comprising ruthenium in the presence of a hydrogen-affording gas under hydrogenation conditions. In this process, the amount of cis-isomers, which is much greater than the amount that would be present at equilibrium, is produced at a reasonable and practical reaction rate. As has been mentioned above, the cis-isomers are thermodynamically

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less favored than the trans-isomers. For example, at a temperature of 350° C., a mixture of cis-decalin and trans-decalin will contain 86.8% trans-decalin and only 13.2% cis-decalin. At the same temperature, a mixture of 1-methyl trans-decalin and 1-methyl cis-decalin will contain 86.2% 1-methyl-trans-decalin and only 13.8% 1-methyl-cis-decalin. In the case of the 2-methyl-decalins at a similar temperature, the mixture will contain 87.6% 2-methyl-trans-decalin and 12.4% 2-methyl-cis-decalin. An equilibrium mixture of the 1-methyl-decalins at 25° C. will contain 98% 1-methyl-trans-decalin and only 2% 1-methyl-cis-decalin. Also, a mixture of the 2-methyl-decalins at 25° C. will contain 97.8% 2-methyl-trans-decalin and 2.2% 2-methyl-cis-decalin. These equilibrium values show that an equilibrium mixture of such polycyclic aromatic hydrocarbons is composed predominantly of the trans-isomers.

It has been found that through the use of the present invention, the product will be composed predominantly of the cis-isomers. It has been found that the increased amount of cis-isomers will be an amount which is greater than 90 weight percent of the sum total of the cis-isomers and the trans-isomers.

It is further believed that the selectivity for producing the cis-oriented isomers is primarily dependent on a catalyst which comprises ruthenium. It is further believed that the mechanism involved in the present process includes the conversion of the fully unsaturated polycyclics having either the cis (as in naphthalene), cis-syn, or cis-anti (as in methyl and dimethyl naphthalene) structures, and that at the higher temperatures the cis-oriented saturated polycyclics are converted to the thermodynamic favored trans-oriented isomers.

The process of this invention utilizes a feed containing substantial amounts of the polycyclic aromatic hydrocarbons; advantageously the polycyclics having 2-3 fused cyclic units including naphthalene, methyl naphthalene, dimethyl naphthalene, and the like, and acenaphthalene and other tricyclic-fused aromatics, and preferably the fused bicyclic aromatic hydrocarbons. This feed may be obtained from the reformat product of various well-known catalytic hydroforming processes such as Ultraforming, Platforming, and the like which employ a platinum catalyst. For example, a reformer naphtha charge boiling in the range from 145° C. to 185° C. can be reformed over a platinum-on-alumina catalyst as described by Forrester, Conn., and Malloy in Petroleum Refinery, vol. 33, No. 4, p. 153 (1954) and in U.S. Patent No. 2,773,008. A fraction boiling in the range between 190° C. and 240° C. is separated from the aromatics-rich portion of the resulting reformat and contains about 90 percent bicyclic aromatics. This fraction is well suited as a feed stock.

The process also has advantages when utilized with partially hydrogenated bicyclic aromatics such as the class identified as tetralins. When further hydrogenated by the process of this invention, some of these tetralins yield even larger amounts of desired cis-isomers than are in the product of the hydrogenated bicyclic aromatics.

The catalyst employed in the present process is a catalyst comprising ruthenium. It can be used as a finely divided pure metal ruthenium powder. However, it can be supported on a nonhydrogenating carrier, such as charcoal or alumina in its various crystalline forms, with or without a solvent, such as acetic acid. It can be used also in its oxide form, but the metallic form is preferred. Advantageously, the ruthenium may be dispersed on a

suitable support, the amount of ruthenium varying from about 0.1 to about 6 weight percent, based on total weight. It is important that the support be a non-hydrogenating support so that hydrogenating components which do not promote the formation of the cis-isomers will not be competing with the ruthenium and thus reduce the conversion to the cis-isomers.

A typical method of preparation of the catalyst is as follows: an alumina support may be impregnated with a solution of ruthenium chloride and the impregnated support may be calcined and steamed to convert the ruthenium to its oxide form.

A catalyst consisting of ruthenium on a carbon support

The hydrogenation was carried out by charging a reactor with the indicated feed and catalyst, after which the reactor was sealed and purged with hydrogen. The contents of the reactor were then heated and stirred. The reactor temperature was thermostatically controlled. After purging with hydrogen, the pressure was increased to a maximum pressure in the order of 1000 p.s.i.g. while the reactor was being heated to the desired temperature. From time to time, additional hydrogen was bled into the reactor to replace that which was used up in the reaction. Samples were taken periodically to follow the extent of reduction in each run, and these were analyzed by gas chromatography. Results from various runs are shown in Table II below:

TABLE II

Run No.	Feed	Catalyst	Temp., (° C.)	Yield of cis- Isomer, percent
1	Naphthalene	5% Ru/C	80	96.8
2	do	5% Ir/C	80	93.7
3	do	5% Pd/C	100	47.4
4	1-methylnaphthalene	0.6% Ru/Al <sub>2</sub> O <sub>3</sub>	200	98
5	do	0.6% Pt/Al <sub>2</sub> O <sub>3</sub>	200	89
6	do	0.6% Rh/Al <sub>2</sub> O <sub>3</sub>	100	85
7	do	0.6% Pd/Al <sub>2</sub> O <sub>3</sub>	200	51
8	2-methylnaphthalene	0.6% Ru/Al <sub>2</sub> O <sub>3</sub>	100	95.6
9	do	0.6% Rh/Al <sub>2</sub> O <sub>3</sub>	100	83
10	do	0.6% Pt/Al <sub>2</sub> O <sub>3</sub>	200	92
11	1,2-dimethylnaphthalene	5% Ru/C	150	90.7
12	do	5% Rh/C	100	75.8
13	do	5% Pd/C	200	31.9
14	Acenaphthene	5% Ru/C	200	95.4
15	do	5% Pd/C	200	36.8

may be purchased from various commercial sources, for example, Engelhard Industries.

A superatmospheric pressure, normally between about 300 and 3000 p.s.i.g. and preferably between about 500 and 2000 p.s.i.g., is employed in the hydrogenation zone. However, lower operating pressures tend to lower the hydrogenation reaction rate, although product composition is relatively unaffected.

The temperature employed for the more favorable yields of the cis-isomers is normally not more than about 300° C. and on the low side is limited only by the reaction rate. Temperatures as low as 25° C. are suitable although the reaction rate is slow. Advantageously, the temperature is between about 100 and about 200° C.

Sufficient hydrogen is made available for saturating the polycyclic aromatic feed by maintaining an excess of hydrogen or other hydrogen-affording gas in the reaction zone. The amount of such gas employed is not critical, although a sufficient amount should be present to assure saturation of the feed. Typically about 1000 to 15,000 and preferably about 2000 to 10,000 standard cubic feet of hydrogen-affording gas per barrel of feed is employed.

The following examples are given in order to illustrate the beneficial effects of carrying out the present process to provide a product rich in the high density, high heat of combustion, cis-oriented isomers. It is to be understood that the following examples are given for illustrative purposes only and are not intended in any way to limit the scope of the present invention.

#### Example 1

Naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 1,2-dimethylnaphthalene, and acenaphthene were individually hydrogenated in the presence of the below-indicated hydrogenation catalyst and under various conditions of temperature as indicated in the following Table II. The amount of cis-isomer in each product was then determined.

In respect to acenaphthene, the amount of the isomer having totally cis-configuration was approximately 88.3% for the ruthenium catalyst and approximately 18.6% for the palladium catalyst.

From the above results, it is evident that the resultant hydrocarbon mixtures had compositions which were made up predominantly of cis-isomers when the hydrogenation component employed was ruthenium. In fact, in each case when ruthenium was used, the amount of cis-isomers obtained was greater than 90 percent of the total amount of cis-isomers and trans-isomers.

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#### Example 2

In this example, tetralin was hydrogenated in the presence of selected catalysts. The catalysts were used individually and each comprised the metal(s) as shown in Table III dispersed on a charcoal support. Each catalyst was made up of 5% metal and 95% support. The hydrogenation members of each catalyst consisted of either individual hydrogenation metals or a mixture of hydrogenation metals. For each catalyst, a specified weight of hydrogenation metals was employed and the numbers represent milligrams. If the hydrogenation member were composed of one hydrogenation metal and 100 mg. of that metal were employed, Table III would show the number 100 in front of the symbol for that metal. If the hydrogenation member were composed of more than one hydrogenation metal, the amount of each hydrogenation metal would appear before the symbol of that particular hydrogenation metal. For example, a catalyst which contained 50 mg. of ruthenium and 50 mg. of palladium dispersed on the charcoal support would be represented in Table III as 50 Ru, 50 Pd.

The reaction in each case was carried out in a specially developed Micro-Magnedash reactor having a reaction-chamber volume of about 5 ml. The hydrogenation was performed by charging the reactor with the specified

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catalyst and feed. The reactor was sealed and purged with hydrogen. The contents of the reactor were heated to the desired temperature and stirred. In each case, 0.5 ml. of tetralin was charged to the reactor. After the hydrogen purge, an initial hydrogen pressure of 1000 p.s.i.g. was created. The temperature employed and the time consumed for each reaction are presented in Table III, along with the conversion of the tetralin and the percent of cis- and trans-isomers of the decalins formed.

support and under the specified temperatures presented in the following Table IV. Each catalyst was composed of 0.6 weight percent of the hydrogenation component on the gamma-alumina. The hydrogenation was performed as discussed in Example 2. Samples removed from the reactor were analyzed by gas chromatography. Please note that the term "cis-isomers" includes cis-syn and cis-anti isomers and the term "trans-isomers" includes trans-syn and trans-anti isomers.

TABLE III  
[Hydrogenation of Tetralin]

Run No.	Catalyst	Temp., °C.	Time, min.	Conversion, percent	Decalin, percent	
					Cis-	Trans-
16	100 Ru	100	3.5	83.6	93.4	6.6
17	100 Pd	100	163	51.6	48.5	51.5
18	50 Ru, 50 Pd	100	4	82	83.2	16.8
19	10 Ru, 90 Pd	100	8.3	88.6	79.3	20.7
20	5 Ru, 95 Pd	100	26	87	76.3	23.7
21	100 Ru	80	4	75.3	94.7	5.3
22	50 Ru, 50 Pd	80	4.5	78	87.4	12.6
23	10 Ru, 90 Pd	80	24	81.2	81.0	19.0
24	100 Pd	80	180	10	49.6	50.4
25	5 Ru, 95 Pd	80	32	76.4	79.4	20.6
26	100 Rh	80	4	74	81.5	18.5
27	10 Rh, 90 Pd	80	16	72	74.4	25.6
28	100 Ir	80	5	79.4	92.0	8.0
29	10 Ir, 90 Pd	80	53	80.3	81.9	18.1
30	50 Ir	80	1.6	12	91.8	8.2
31	50 Ir	80	4	27.4	91.8	8.2
32	50 Ir	80	7.3	46.8	91.5	8.5
33	50 Ir	80	19	87.7	93.7	6.3
34	100 Ir	25	1,200	15	92.5	7.5
35	20 Ir, 180 Pd	25	1,400	20.3	80.9	19.1
36	100 Pt	25	480	2.2	84.0	16.0
37	20 Pt, 180 Pd	25	1,400	4.6	53.9	46.1
38	100 Rh	25	7	78.5	88.9	11.1
39	10 Rh, 90 Pd	25	210	50	82.2	17.8
40	10 Ru, 90 Pd	25	108	35.5	83.5	16.5
41	100 Ru	25	6	79.8	94.5	5.5
42	100 Pd	25	1,260	5.6	46.9	53.1

As shown in the above table, the catalyst which provided the greatest percentage of the cis-isomers at a reaction temperature of 100° C. was the catalyst which consisted of 100 mg. of ruthenium dispersed on the charcoal. This catalyst was far superior to the catalyst which consisted of 100 mg. of palladium on charcoal. Although the catalysts which had ruthenium mixed with palladium showed improved conversion of the tetralin and a higher concentration of the cis-isomer in the product than when the hydrogenation component consisted solely of palladium, the resulting amount of the cis-isomers did not equal the high percentage obtained with the catalyst containing ruthenium as the sole hydrogenation component. This phenomena was shown also by the data obtained from the runs which employed a reaction temperature of 80° C. Likewise, when the reaction temperature was 25° C., the greatest amount of cis-isomer was obtained with the use of ruthenium as the sole hydrogenation component.

#### Example 3

Individual methyltetralins were hydrogenated in the presence of a catalyst which was composed of the below-indicated hydrogenation component on a gamma-alumina

TABLE IV

	Feed	Catalyst	Temp., °C.	Cis- isomers, percent	Trans- isomers, percent
55	1-methyltetralin	Ru	100	94.6	5.4
		Rh	100	85.0	15.0
		Ir	200	85.1	14.9
		Pt	200	79.3	20.7
		Pd	200	55.0	45.0
60	5-methyltetralin <sup>1</sup>	Ru	100	97.5	2.5
		Rh	100	73.6	26.4
		Ir	200	68.5	31.5
		Pt	200	75.4	24.6
		Pd	200	52.3	47.7
65	2-methyltetralin <sup>2</sup>	Ru	100	94.8	5.2
		Rh	100	78.5	21.5
		Ir	200	43.6	56.4
		Pt	200	72.8	27.2
		Pd	200	48.2	51.8
70	6-methyltetralin	Ru	100	94.7	5.3
		Rh	100	86.5	13.5
		Ir	200	82.4	17.6
		Pt	200	86.3	13.7
		Pd	200	55.2	44.8

<sup>1</sup> Plus 0.8-1-MeT impurity.

<sup>2</sup> Plus 2-6-MeT impurity.

It is clearly shown that in each case when the methyltetralin was contacted with the ruthenium-on-alumina catalyst, the resulting hydrocarbon mixture contained an amount of the cis-isomers which was greater than 90% of the total amount of cis-isomers and trans-isomers.

In the above examples, only one hydrogenation metal gave consistently mixtures which contained cis-isomers in an amount greater than 90% of the total amount of cis-isomers and trans-isomers present. This hydrogenation metal was ruthenium.

What is claimed is:

1. A process for the preparation of an increased amount of cis-isomers of hydrogenated polycyclic aromatic hydrocarbons having 2-3 fused cyclic units wherein said increased amount is greater than 90% of the total amount of cis-isomers and trans-isomers which process comprises contacting polycyclic aromatic hydrocarbons with a catalyst consisting essentially of ruthenium on a non-hydrogenating support in the presence of a hydrogen-affording gas under hydrogenation conditions, including a temperature between about 25° C. and about 200° C. and a superatmospheric pressure which does not exceed 3000 p.s.i.g.

2. The process of claim 1 wherein said polycyclic aromatic hydrocarbons have 2 fused cyclic units.

3. The process of claim 1 wherein said polycyclic aromatic hydrocarbons include methylnaphthalene.

4. The process of claim 1 wherein said polycyclic aromatic hydrocarbons include dimethylnaphthalene.

5. The process of claim 1 wherein said polycyclic aromatic hydrocarbons include acenaphthene.

6. The process of claim 1 wherein said catalyst consists of about 0.1 to about 6 weight percent ruthenium on a non-hydrogenating support and wherein said temperature is between about 100° C. and about 200° C. and said pressure is between about 500 p.s.i.g. and about 3000 p.s.i.g.

10 7. The process of claim 6 wherein a product rich in cis-isomers of the hydrogenated polycyclic aromatic hydrocarbons is recovered.

15 8. The process of claim 6 wherein said polycyclic aromatic hydrocarbons comprise tetralin.

9. The process of claim 6 wherein said polycyclic aromatic hydrocarbons comprise a mixture of methyltetralins.

#### References Cited

#### UNITED STATES PATENTS

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, TABLE II, fourth column, line 4 thereof, for "200" read -- 100 --; column 5, TABLE III, second column, last line thereof, for "100 Pd" read -- 200 Pd --; column 6, TABLE IV, footnote 1 thereof, for "0.8" read -- 0.8% --; same table, footnote 2 thereof, for "2" read -- 2% --.

Signed and sealed this 25th day of February 1969.

(SEAL)

Attest:

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Commissioner of Patents