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NONCATALYTIC ISOMERIZATION OF AROMATIC COMPOUNDS

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This invention relates to the isomerization of aromatic compounds containing at least one aliphatic side chain comprising more than two carbon atoms. It is more particularly concerned with the isomerization, in the absence of added catalyst, of alkyl aromatic hydrocarbons.

The isomerization of organic compounds, and of hydrocarbons in particular, has been studied extensively. Investigators in this field have believed that the isomerization reactions must be conducted in the presence of an isomerization catalyst. In contrast, we have found that certain types of compounds can be isomerized in the absence of added catalyst.

In a broad aspect, our invention comprises isomerizing an aromatic compound containing at least one aliphatic side chain comprising more than two carbon atoms by subjecting the same in the absence of added catalyst to an elevated temperature under a high pressure for a time sufficient to effect said isomerization.

In one embodiment our invention relates to a process which comprises subjecting an aromatic compound containing at least one aliphatic side chain comprising more than two carbon atoms, in the absence of added catalyst, to an elevated temperature, and a substantial superatmospheric pressure, and for a time such that isomerization is effected.

In a more specific embodiment our invention relates to a process which comprises subjecting a carbocyclic aromatic compound having an alkyl group comprising more than two carbon atoms attached to a nuclear carbon atom, in the absence of added catalyst, to an elevated temperature, a substantial superatmospheric pressure, and for a time such that isomerization is effected.

In another specific embodiment our invention relates to a process for isomerizing an alkylbenzene in which the alkyl group contains more than two carbon atoms, said process comprising heating said alkylbenzene at a substantial superatmospheric pressure in the absence of added catalyst until isomerization is at least partially complete.

In still another specific embodiment our invention relates to a process which comprises subjecting a heterocyclic aromatic compound containing at least one aliphatic side chain comprising more than two carbon atoms, in the absence of added catalyst, to an elevated temperature, a substantial superatmospheric pressure, and for a time sufficient to effect isomerization of said heterocyclic aromatic compound.

The compounds that may be isomerized in accordance with our process comprise aromatic compounds having attached to a nuclear carbon atom at least one aliphatic side chain, said side chain containing more than two carbon atoms. By the term aromatic compound we mean to

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include not only substituted benzenes, naphthalenes, and derivatives thereof, but also all compounds containing a stable ring or nucleus such as is present in benzene and which possesses unsaturation in the sense that benzene does. Consequently it can be seen that the term aromatic compound, in the sense in which it is used in the specification and the appended claims, includes not only carbocyclic compounds but also heterocyclic compounds having stable nuclei.

The carbocyclic aromatic compounds may have a benzene, naphthalene, anthracene, etc., nucleus. The heterocyclic aromatic compound may have a pyridine, furan, thiophene, pyrrole, pyrazole, etc., nucleus. In addition, the aromatic compounds contemplated for use in our process may contain both a carbocyclic and a heterocyclic ring such as is found in indole and in carbazole. Also, the aromatic compounds may contain a benzene nucleus and a cycloalkane nucleus such as is found in tetralin and in indan.

As hereinbefore stated, the aromatic compounds that may be employed in our process contain at least one aliphatic side chain comprising more than two carbon atoms. The chain will contain three or more carbon atoms, which may be in straight chain or branched chain relation such as the normal butyl radical or the isobutyl radical in normal butylbenzene and isobutylbenzene, respectively. It is preferred that the chain contain no carbon-carbon unsaturation, for aromatic compounds containing a side chain in which an ethylenic group and/or an acetylenic group is present tend to polymerize under the conditions employed in our isomerization process. The side chain preferably is an alkyl group, although one or more of the hydrogen atoms on the alkyl group may be substituted with other radicals such as cycloalkyl radicals, hydroxyl radicals, alkoxy radicals, halogen radicals, and the like. In aromatic compounds of the type exemplified by indan, the aliphatic side chain should be attached to the aromatic nucleus.

The aromatic ring in the compounds herein referred to may contain other substituents such as a chloro group, a methoxy group, an ethoxy group, a nitro group, and the like.

Alkyl aromatic hydrocarbons, particularly alkylbenzenes, in which the alkyl group contains more than two carbon atoms, constitute the preferred compound for use in our process. If an alkylbenzene such as cumene is subjected to isomerization in accordance with our invention, the principal product, under selected conditions of operation, will be one in which the side chain has isomerized. However, there occasionally will be some migration of hydrocarbon groups such as methyl groups from the alkyl side chain to new positions along the nucleus.

Pressure is one of the important variables in

our process. The isomerization reactions with which our invention is concerned ordinarily proceed with the best yields when conducted at substantial superatmospheric pressures. We have obtained excellent results in the range of 3000 to 12000 pounds per square inch. Higher pressures are not only operable, but in many cases they are advantageous from the standpoint of increased yields and selectivity of the reaction. The lower pressure limit with most reactants usually is about 1000 pounds per square inch. However, it is to be understood that the lower operable pressure limit will depend upon the particular aromatic compound that is being isomerized; for the more active compounds will isomerize at lower pressures than those that are not so active. Consequently, the foregoing pressure ranges are to be taken as indicative of the general range throughout which our isomerization reactions will occur.

The temperature at which our process is conducted is dependent to a large extent upon the reactants that are being employed. In general, the temperatures will be greater than about 400° C., but should not be so great that appreciable cracking and decomposition reactions take place. The preferred temperature range with alkylbenzene hydrocarbon is from about 475° to about 525° C.

Additional details and advantages of our invention will be apparent from the following examples, which are given for purposes of illustration and not for purposes of limitation.

EXAMPLE I

In four continuous-type experiments, cumene (isopropylbenzene) was passed through a reaction tube at hourly liquid space velocities ranging from 1.0 to 1.45, at pressures ranging from 3000 to 12,000 p. s. i., and at temperatures ranging from 475° C. to 528° C. The products from these experiments were distilled and the fractions were analyzed by the infra-red method. The operating conditions and results are shown in the following table.

TABLE I

Isomerization of cumene

Experiment No.	1	2	3	4
Pressure, p. s. i.	3,000	12,000	12,000	12,000
Temperature, ° C.	475	479	501	528
Cumene Charged, gr.	182	195	177	314
H. L. S. V.	1.05	1.00	1.35	1.46
Yields:				
Liquid Product, g.	181.9	190.4	170.9	296
Cond. gas, gr.	0.0	0.0	0.0	1.6
Non Cond. gas, liters	0.0	1.5	5.450	21.8
Liquid Product, Wt. Percent:				
Benzene	(1)		1.0	2.7
Toluene	(1)	0.9	4.4	16.4
Ethylbenzene	(1)	3.1	9.0	16.3
Cumene	(1)	78.0	55.5	25.5
n-propylbenzene	(1)	12.7	14.8	13.8
Higher boiling product	(1)	5.4	15.2	25.3
Yield on Recycle Basis, Wt. Percent:				
Gaseous product	(1)	2.8	5.5	7.8
Benzene	(1)	0.0	2.1	3.3
Toluene	(1)	3.9	9.3	20.3
Ethylbenzene	(1)	13.7	19.2	20.0
n-Propylbenzene	(1)	55.9	31.6	17.2
Higher boiling product	(1)	23.7	32.3	31.4
Analysis of Noncond. Gas, Mol Percent:				
H_2	(1)	10.4	2.8	0.6
CH_4	(1)	70.0	76.3	77.8
C_2H_4	(1)	9.2	13.2	15.0
C_2H_6	(1)	3.7	0.5	0.5
C_3H_6	(1)	5.4	6.5	5.0
C_3H_8	(1)	1.3	0.6	1.0
C_4H_{10}	(1)	0.0	0.1	0.1

[1] No reaction.

At 12,000 p. s. i., the per pass isomerization of isopropylbenzene to n-propylbenzene was 12.7% at 479°, 14.8% at 501°, and 13.8% at 528° C. Raising the temperature did not alter to any extent the yield of n-propylbenzene per pass, but at the higher temperatures excessive side reactions took place so that on the recycle basis the yield of n-propylbenzene is higher at the lower temperatures. On a recycle basis the yield of n-propylbenzene at 479°, 501°, and 528° C., respectively, were 55.9%, 31.6%, and 17.2%.

Pressure was found to have a very marked effect on this reaction. At 3000 p. s. i. and 475° C., cumene remained unchanged; whereas at 12,000 p. s. i. and 479° C., 12.7% of the cumene was converted to n-propylbenzene per pass.

As hereinbefore stated, excessive side reactions took place at 528° C. and 12,000 p. s. i. and 25.3% of the product was higher boiling than n-propylbenzene. In this experiment some of the higher boiling compounds were characterized. The compounds found to be present in this higher boiling fraction were naphthalene, α-methylnaphthalene, β-methylnaphthalene, and p-diphenylbenzene.

EXAMPLE II

The operating conditions and results of six batch-type experiments in which cumene and normal propylbenzene were subjected to elevated temperatures in a rotating autoclave are shown in the following table. In three of the experiments, normal propylbenzene rotated in an autoclave four times ranging from about 2.5 to about 3.5 hours, at temperatures ranging from 350° C. to 400° C., and at pressures ranging from about 20 to 41 atmospheres. In the other three experiments, cumene was subjected to approximately the same conditions. The runs were made by sealing 60 grams of cumene or normal propylbenzene in a 330 milliliter autoclave and rotating at the desired temperature.

TABLE II

Isomerization of cumene and n-propylbenzene

Experiment No.	5	6	7	8	9	10
Temperature, ° C.	350	375	400	375	400	425
Max. pressure, atmos.	20	35	41	35	42	50
Hours	2.5	3.0	3.5	4.0	4.0	4.0
Charge:						
Cumene, gr.				60	60	60
n-Propylbenzene, gr	60	60	60			
Results:						
Liquid product, gr.	56.6	54.8	54.8	56.9	58.0	56.5
Noncond. gas, cc.	0.0	200	[1] 2,220	0.0	250	[2] 1,280
Loss	3.4	5.2	5.2	3.1	2.0	3.5
Liquid Product consists of, Wt. Percent:						
Toluene			8.6			2.5
Ethylbenzene		5.2	4.8		2.2	14.5
Cumene	1.2	1.3	6.4		95.6	70.0
n-Propylbenzene	98.8	90.6	61.4		0.2	6.8
Higher boiling product		2.9	19.1		2.0	6.2

[1] H_2=5.4, CH_4=82.4, C_2H_4=3.1, C_2H_6=6.1, C_3H_6=0.7, C_3H_8=2.2.
[2] H_2=13.5, CH_4=74.9, C_2H_4=1.7, C_2H_6=4.1, C_3H_6=1.5, C_3H_8=3.9.

The results of these experiments show that the thermal or noncatalytic isomerization of alkylaromatic hydrocarbons is an equilibrium reaction, i. e., a normal compound can be isomerized to the iso compound and the iso compound can be isomerized to the normal compound. For a given degree of conversion, with the indicated reactants, it appears that the reaction temperature must be about 25° C. higher in the case of the iso compound.

A comparison of the results obtained in the continuous-type runs were those obtained in the batch-type runs, shows that in the latter isomerization was obtained at lower temperatures and pressures. This presumably is due to the

greater length of time at the reaction temperature in the batch-type runs. On the other hand, the yields in the batch-type runs are appreciably smaller. These yields can be increased by increasing the pressure and the reaction temperature.

EXAMPLE III

Normal butylbenzene and secondary butylbenzene in two different experiments were passed through a reaction tube at an hourly liquid space velocity of 1.5, a temperature of 475° C., and a pressure of 12,000 p. s. i. In the case of the normal butylbenzene, the principal product was secondary butylbenzene in yields amounting to 13.5% per pass. In the experiment in which secondary butylbenzene was employed as the charging stock, the principal product was normal butylbenzene in yields amounting to 11.3%.

EXAMPLE IV

1-chloro-3-secondary butylbenzene was passed through a reaction tube at an hourly liquid space velocity of 1.5, a temperature of 475° C., and a pressure of 12,000 p. s. i. The principal product was 1-chloro-3-normal butylbenzene. The yield of this compound amounted to 12.9%.

EXAMPLE V

Para isopropylmethoxybenzene was passed through a reaction zone maintained at a temperature of 475° C. and a pressure of 12,000 p. s. i. at a space velocity of 1.4. A yield of 14.3% of para normal propylmethoxybenzene was obtained.

EXAMPLE VI

A yield of 9.8% of normal propylpyridine was obtained by passing isopropylpyridine through a reaction tube maintained at a temperature of 475° C., a pressure of 12,000 p. s. i. at an hourly liquid space velocity of 1.4.

From the foregoing description of our invention, it can be seen that we have invented a novel and effective method of isomerizing certain aromatic compounds containing aliphatic side chains in the absence of added catalysts.

We claim as our invention:

1. A process which comprises subjecting an aromatic compound having an alkyl side chain containing more than two carbon atoms to thermal isomerization at a temperature of from about 400° to about 525° C., a pressure of at least 3000 pounds per square inch and an hourly liquid space velocity of from about 1.0 to about 1.5.

2. A process which comprises subjecting a carbocyclic aromatic compound having attached to a nuclear carbon atom an alkyl group of more than two carbon atoms to thermal isomerization at a temperature of from about 400° to about 525° C., a pressure of at least 3000 pounds per square inch and an hourly liquid space velocity of from about 1.0 to about 1.5.

3. A process which comprises subjecting an aromatic hydrocarbon having attached to a nuclear carbon atom an alkyl group of more than two carbon atoms to thermal isomerization at a temperature of from about 400° to about 525° C., a pressure of at least 3000 pounds per square inch and an hourly liquid space velocity of from about 1.0 to about 1.5.

4. A process which comprises subjecting an alkylbenzene in which the alkyl group contains more than two carbon atoms to thermal isomerization at a temperature of from about 400° to about 525° C., a pressure of at least 3000 pounds per square inch and an hourly liquid space velocity of from about 1.0 to about 1.5.

5. The process of claim 4 further characterized in that said alkyl group is of straight chain configuration.

6. The process of claim 4 further characterized in that said alkyl group is of branched chain configuration.

7. The process of claim 4 further characterized in that said alkylbenzene is normal propylbenzene.

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