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3,308,178

PROCESS FOR THE PARTIAL REDUCTION
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This invention relates to a process for the partial reduction of aromatic compounds. More particularly, it relates to an improved process for the production of cyclohexenes by partial reduction of corresponding benzenes.

Several methods are available in the art for the partial reduction of aromatic compounds, e.g., benzene and substituted benzenes. U.S. Patent 2,182,242, issued Dec. 5, 1939, to Wooster, describes a low-temperature reduction of benzene by contact with sodium and liquid ammonia in the presence of added excess acidic material such as water or alcohol to produce cyclohexadiene. A recent modification of this process is found in French Patent 1,363,841, granted May 4, 1964, to Yamaguchi et al. wherein utilization of amounts of water or alcohol less than equivalent to the amount of alkali metal present results in the formation of cyclohexene. It is also known, see Benkeser, J. Am. Chem. Soc., 3230 (1955), that a similar reduction may be effected by treating benzene with lithium in primary amine solvent to obtain a mixture of cyclohexene and cyclohexane.

It is an object of the present invention to provide an improved process for the partial reduction of mononuclear aromatic hydrocarbons. More particularly, it is an object to provide an improved process for the partial reduction of benzene and certain substituted benzenes. A specific object is to provide an improved process for the partial reduction of alkylbenzenes.

It has now been found that these objects are accomplished by reacting benzene or substituted benzenes with certain alkali metals in a solvent comprising at least a major proportion of primary amine. In contrast with similar processes of the prior art, the process of the invention is characterized by an increased reaction rate which enables less vigorous reaction conditions to be employed, and, when substituted benzenes are utilized as reactants, by an increased yield and a more favorable isomer distribution of reduced product.

The aromatic reactants suitably employed in the process of the invention are mononuclear aromatic hydrocarbons containing a single six-membered aromatic ring. Suitable aromatic hydrocarbons contain from 6 to 20 carbon atoms and are characterized as benzene and aliphatic hydrocarbyl-substituted benzene. Although aliphatic hydrocarbyl substituents which contain carbon-carbon unsaturation are in part operable, such unsaturation is customarily hydrogenated during the course of the reaction and no advantage is gained by utilization of benzenes containing side-chain unsaturation. Best results are obtained when the aliphatic hydrocarbyl substituents are alkyl, including cycloalkyl, having from 1 to 14 carbon atoms. Although the process of the invention is suitably employed when the central benzene nucleus possesses a plurality of alkyl substituents, preferred aromatic hydrocarbon reactants are unsubstituted benzene or benzene substituted with from 1 to 3 alkyl substituents. The preferred aromatic reactants are therefore characterized as non- to tri-alkylbenzene having from 6 to 20 carbon atoms wherein any alkyl substituent(s) are alkyl, including cycloalkyl, of from 1 to 14 carbon atoms. Illustrative of such preferred reactants are benzene, toluene, ethylbenzene, cumene, tert-butylben-

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zene, tert-butyltoluene, p-diethylbenzene, m-diisopropylbenzene, xylene, o-di-n-propylbenzene, cyclohexylbenzene, p-cyclopentyltoluene, hexylbenzene, mesitylene, pseudocumene, 1,3,5-tripropylbenzene, n-butylbenzene, octylbenzene, m-octylethylbenzene, decylbenzene, dodecylbenzene, (3-methylcyclohexyl)benzene and tetradecylbenzene. In general, acyclic alkyl substituents are preferred over analogous cycloalkyl substituents, and especially preferred is non- to mono-alkylbenzene wherein any alkyl is acyclic alkyl of from 1 to 4 carbon atoms.

A somewhat special case exists with regard to Tetralin, which is herein considered to be within the contemplated scope of the dialkylbenzenes of the invention, thereby adding the proviso that when the non- to tri-alkylbenzene is 1,2-dialkylbenzene, the alkyl moieties may together form a divalent alkylene moiety having 4 carbon atoms.

The alkali metal employed in the process of the invention is a member of Group I of the Periodic Table having an atomic number from 19 to 37, that is, potassium or rubidium. While it is known that lithium will afford similar reduction of the aromatic reactant, sodium or cesium are not suitable in the amine solvents utilized, these metals leading to limited or no conversion of the aromatic reactant. Largely for economic reasons, the use of potassium is preferred over an analogous utilization of rubidium.

Without wishing to be bound by any particular theory, it appears probable that the alkali metal reacts directly with the aromatic reactant to produce a mono-metal derivative, e.g., a benzene free-radical anion, which subsequently reacts with the solvent to introduce hydrogen into the aromatic ring. Subsequent additional reactions result in the formation of the desired cyclohexene product. Thus, four gram-atoms of alkali metal are required to effect complete conversion of each mole of aromatic reactant. The alkali metal is preferably employed in amounts equivalent to or in excess over the amount of aromatic reactant, although lesser amounts of alkali metal may be employed if complete conversion of the aromatic reactant is not required. Thus, ratios of gram-atoms of alkali metal to moles of aromatic reactant from about 2:1 to about 10:1 are suitable, however, ratios of gram-atoms of alkali metal to moles of aromatic reactant from about 4:1 to about 8:1 are preferred. The alkali metal of atomic number from 19 to 37 is employed as a pure substance or as a mixture or alloy with the other member of the class. Mixtures of potassium and rubidium in all proportions are suitable. Rather unexpectedly, it has been found that mixtures of alkali metal of atomic number from 19 to 37 with alkali metals that are unsuitable when utilized singly exhibit power to reduce the aromatic reactant beyond that calculated for the amount of alkali metal of atomic number from 19 to 37 present in the mixture. For example, although sodium employed alone converts little or none of the aromatic reactant, a mixture of sodium and potassium results in greater conversion of the aromatic reactant than can be attributed to the potassium present in the mixture. Thus, mixtures of singly suitable alkali metal, e.g., potassium or rubidium, with singly unsuitable alkali metal, e.g., sodium or cesium, may be employed and such mixtures may contain any convenient proportion of singly suitable and singly unsuitable alkali metals. To obtain satisfactory results through utilization of such a mixture, it is desirable that amounts of such mixture be employed sufficient to provide at least one gram-atom of alkali metal of atomic number from 19 to 37 for each mole of aromatic compound utilized. In the modification of the process of the invention employing mixed suitable and unsuitable alkali metal, ratios of gram-atoms of total alkali metal to moles of aromatic reactant having an

atomic number from 11 to 55 from about 2:1 to about 10:1 are satisfactory, provided that the mixture contain at least 1 gram-atom of alkali metal having an atomic number from 19 to 37 for each mole of the aromatic reactant employed.

The process of the invention is conducted by contacting the non- to tri-alkylbenzene with alkali metal in the presence of a liquid aliphatic amine. Although aliphatic secondary amines and aliphatic poly(primary amines) are in part operable, best results are obtained when the amine is an aliphatic primary amine, particularly a lower alkylamine of from 1 to 4 carbon atoms as exemplified by methylamine, ethylamine, n-propylamine, n-butylamine, isopropylamine, sec-butylamine and isobutylamine. Best results are obtained when the amine is an n-alkylamine, particularly n-alkylamine of from 1 to 2 carbon atoms, i.e., methylamine and ethylamine. The amine employed in the process of the invention appears to serve several functions. The amines serve as a solvent for the organic and inorganic reactants, and also serves as a source of the hydrogen introduced onto the benzene ring of the aromatic reactant. The use of an amine provides a substantial advantage for the present process over similar processes of the prior art. Certain of these processes, e.g., that of U.S. 2,182,242, employ reaction systems containing hydroxylic components, e.g., water or alcohol. In such processes, the alkali metal-containing product is the hydroxide or alkoxide from which the alkali metal is not easily regenerated. The effective loss of alkali metal precludes economical utilization of these processes on a commercial basis. In the present process when amine is employed as sole solvent, the alkali metal product is an amide, e.g., from the reaction of potassium in methylamine is obtained potassium methanide. From such an alkylamide product, the alkali metal is recovered as by amine exchange with ammonia to produce alkali metal amide, e.g., potassium amide, followed by hydrogenation of the amide to the corresponding alkali metal hydride and pyrolysis of the hydride to liberate the elemental alkali metal. In the modification of the process of the invention wherein alkylamine is employed as sole solvent, molar ratios of amine to the aromatic reactant from about 7:1 to about 50:1 are generally satisfactory, although molar ratios of amine solvent to aromatic reactant from about 12:1 to about 30:1 are preferred. The amine is preferably employed in a form substantially free of hydroxylic materials, e.g., water, alcohol, or carboxylic acid, which result in the recovery of alkali metal in the form of undesirable by-products. Although small amounts, e.g., up to about 5% by weight based on total solvent, of hydroxylic material may be tolerated without losing the advantages of the process of the invention, the solvent employed is preferably free from hydroxylic compound.

In an alternate modification of the process of the invention, solvent is provided as a mixture of amine with a limited amount of ammonia. The presence of substantial quantities of ammonia in the reaction solvent has a deleterious effect on the process of the invention through lowering of the reaction rate, lowering of product yield when alkylated benzenes are employed as the aromatic reactant, and promotion of an undesirable isomer distribution of alkylated cyclohexene produced by reduction of such alkylated benzenes. When limited amounts of ammonia are employed in the reaction solvent, these undesirable effects are minimized and are compensated by the recovery of the alkali metal as the amide, rather than the alkylamide, from which the alkali metal is more easily regenerated as by the procedure discussed above. The molar amount of ammonia to be employed in a solvent comprising a mixture of amine and limited ammonia is preferably not greater than three times the gram-atomic amount of alkali metal present in the reaction system, and best results are obtained when the molar ratio of any ammonia present to alkali metal is substantially stoichiometric,

that is, a molar ratio of about 1:1. The solvent employed in the present process therefore comprises alkylamine optionally containing ammonia. When mixed amine-ammonia solvent is employed, amounts of ammonia up to about 40% mole based upon total solvent are suitable, although amounts of ammonia up to about 25% mole on the same basis are preferred.

The process of the invention is operable in the presence of inert diluents such as saturated hydrocarbons, e.g., hexene, heptene, cyclohexane and the like. The presence of such diluents, however, offers no advantage to compensate for the increased difficulty of product separation and in the preferred modification of the invention, no inert diluents are employed.

The process is conducted at a somewhat elevated temperature. The advantages of utilization of an amine solvent are illustrated by a lowered temperature requirement when compared to processes wherein ammonia is employed as the sole solvent. Suitable reaction temperatures are from about 15° C. to about 110° C., with the temperature range from about 20° C. to about 100° C. being generally preferred, and the temperature range from about 30° C. to about 80° C. being particularly satisfactory. The reaction is conducted at pressures which are atmospheric, subatmospheric or superatmospheric as long as the reactants are maintained substantially in the liquid phase. Typical reaction pressures vary from about 5 atmospheres to about 50 atmospheres although reaction pressures from about 10 atmospheres to about 40 atmospheres are most customary.

Subsequent to reaction, the product mixture is separated and the desired cyclohexene product is recovered by conventional means such as fractional distillation, selective extraction, crystallization and the like.

The product of the present process is a non- to tri-alkylcyclohexene illustratively produced by the addition of four atoms of hydrogen to the aromatic ring of the non- to tri-alkylbenzene as previously defined. For example, from reaction of benzene is obtained cyclohexene, and from toluene is obtained a mixture of 1-methylcyclohexene, 3-methylcyclohexene, and 4-methylcyclohexene. A particular advantage of the present process lies in the favorable isomer distribution resulting from the reduction of alkylbenzenes thereby. For example, 1-methylcyclohexene is a most desirable isomer resulting from toluene reduction, due to the known pyrolyzability of this isomer to ethylene and isoprene. From reductions employing lithium and amine, the percentage of 1-methyl isomer observed in the product mixture approximates 65%. However, by the present the selectivity toward production of the 1-methylcyclohexene isomer is often over 90%.

The cyclohexene products of the invention are useful as chemical intermediates. The non-alkyl product, cyclohexene, is a chemical of commerce and has particular utilization as a precursor for α,ω -dicarboxylic acids, ω -aminocarboxylic acids, polyesters, polyamides and the like.

To further illustrate the improved process of the invention, the following examples are provided. It should be understood that the details thereof are not to be regarded as limitations, as they may be varied as will be understood by one skilled in this art.

EXAMPLE I

A series of partial reductions of benzene were attempted employing methylamine and various alkali metals. In each case, the reactants were charged to an autoclave which was then sealed and maintained at the reaction temperature for the indicated period, after which the reactor was cooled and opened and the product mixture removed therefrom. The organic materials were separated from the inorganic products by distillation and the product composition was determined by gas-liquid chromatography. The results of this series are shown in Table I.

TABLE I

Benzene, Moles	Metal, g.-atoms	Amine, Moles	Temp., ° C.	Time, Hrs.	Conv. of Benzene, Percent	Selectivity to Cyclohexene
0.1-----	Na, 0.4-----	2.0	60	15.5	1	100
0.1-----	K, 0.4-----	2.0	61	0.66	39.2	100
0.026-----	K, 0.038-----	1.0	28; 50	1.3; 0.5	5.7	100
0.033-----	Rb, 0.034-----	1.0	26; 46	1.5; 1.0	4.8	100
0.031-----	Cs, 0.038-----	1.0	32; 53	1.8; 0.8	0	0

EXAMPLE II

By a procedure similar to that of Example I, benzene was reacted with potassium in the presence of various amines. In each case, 0.1 mole of benzene was contacted with 0.4 gram-atom of potassium. The results are shown in Table II.

TABLE II

Amine, Moles	Temp., ° C.	Time, Hrs.	Conversion of Benzene	Selectivity to Cyclohexene
CH ₃ NH ₂ , 2.0-----	61	0.66	39.2	100
C ₂ H ₅ NH ₂ , 1.7-----	65	7.2	15.2	100
n-C ₄ H ₉ NH ₂ , 0.71-----	60	3.5	11.7	100
(CH ₃ NH ₂) ₂ , 0.69-----	61-65	4.0	6.7	-----
(CH ₃) ₂ NH, 2.2-----	60	8	3	100

EXAMPLE III

To illustrate the difference in isomer distribution obtained through utilization of the present process, experi-

EXAMPLE IV

By a procedure similar to that of Example I, experiments were conducted employing a mixed methylamine-ammonia solvent, 0.1 mole of toluene and 0.4 gram-atom of potassium. The organic product was a mixture of methylcyclohexene isomers and the inorganic product

was potassium amide. The results are shown in Table IV wherein selectivity refers to the percentage of 1-methylcyclohexene in the product mixture.

TABLE IV

CH ₃ NH ₂ , Moles	NH ₃ , Moles	Temp., ° C.	Time, Hrs.	Conversion of Toluene, Percent	Selectivity
2.1-----	0.44	57-60	0.5	49.3	90.7
1.9-----	0.47	20-24	5	51.3	91
1.9-----	0.88	53-60	1.5	58.7	89.9

ments involving reduction of toluene were conducted employing lithium and potassium as the alkali metal. The procedure employed was similar to that of Example I. The results are shown in Table III wherein selectivity refers to the percentage of 1-methylcyclohexene present in the product mixture.

TABLE III

Toluene, moles	Metal, g.-atoms	Methylamine, moles	Temp., ° C.	Time, Hrs.	Conversion of Toluene, Percent	Selectivity
0.102-----	Li, 0.4-----	1.9	60	3	43.1	66.3
0.1-----	K, 0.4-----	1.9	60	0.83	48.5	83.7
0.1-----	K, 0.4-----	1.9	60-74	0.5	47.1	90

EXAMPLE V

To illustrate the effect of employing a mixture of suitable alkali metal with alkali metal that is unsuitable when employed alone, mixtures of sodium with potassium or rubidium were employed to react with 0.1 mole of benzene in 2 moles of methylamine. It should be noted that

the amount benzene reduced is greater than that allowable from reaction of the potassium or rubidium alone. The results of these experiments are shown in Table V.

TABLE V

Metal, g.-atom	Temp., ° C.	Time, Hrs.	Conv. of Benzene	Selectivity to Cyclohexene
Na, 0.36; K, 0.05-----	60	8	31.8	100
Na, 0.34; K, 0.05-----	100-106	5	41.7	100
Na, 0.35; Rb, 0.053-----	56-60	4.5	23.3	100

7 EXAMPLE VI

By a procedure similar to that of Example I, experiments were conducted employing 0.1 mole of various alkyl benzenes, 0.4 mole of alkali metal and 2.0 moles of methylamine as solvent. The results are shown in Table VI wherein selectivity refers to the percentage of 1-alkylcyclohexene in the product mixture.

TABLE VI

Alkylbenzene	Metal	Temp., ° C.	Time, Hrs.	Conversion of Alkylbenzene	Selectivity
Cumene.....	K	63-67	3	62	83.4
t-Butylbenzene.....	K	60	2	75.5	86.1
t-Butylbenzene.....	Li	60	8	59.8	69.6

EXAMPLE VII

By a procedure similar to that of Example I, experiments were conducted employing 0.1 mole of various di- to tri-alkylbenzenes, 0.4 mole of potassium and 2.0 moles of methylamine. The results are shown in Table VII wherein selectivity refers to the percentage of the listed product in the product mixture.

TABLE VII

Alkylbenzene	Temp., ° C.	Time, Hrs.	Conversion of Alkylbenzene	Selectivity, Product
o-Xylene.....	60-68	1.25	33.6	83, 1,2-dimethylcyclohexene.
Mesitylene.....	60-69	2	50.4	100, 1,3,5-trimethylcyclohexene.
Tetralin.....	60-70	2.3	40.3	95, 9,10-octalin.

I claim as my invention:

1. The process of producing cyclohexenes by intimately contacting non- to tri-alkylbenzenes of 6 to 20 carbon atoms with from about 2 gram-atoms to about 10 gram-atoms of alkali metal of atomic number from 11 to 55 per mole of said non- to tri-alkylbenzene wherein at least one gram-atom of said alkali metal per mole of said non- to tri-alkylbenzene is alkali metal of atomic number from 19 to 37, in solvent comprising from about 7 moles to about 50 moles per mole of said non- to tri-alkylbenzene of lower alkylamine of from 1 to 4 carbon atoms and up to about 40% mole based on total solvent of ammonia, in the liquid phase at a temperature from about 15° C. to about 110° C.

2. The process of producing cyclohexenes by intimately contacting non- to tri-alkylbenzene of from 6 to 20 carbon atoms with from about 2 gram-atoms to about 10 gram-atoms of alkali metal of atomic number from 11 to 55 per mole of said non- to tri-alkylbenzene wherein at least one gram-atom of said alkali metal per mole of said non- to tri-alkylbenzene is potassium, in solvent comprising from about 7 moles to about 50 moles per mole of said non- to tri-alkylbenzene of alkylamine of from 1 to 2 carbon atoms and up to about 25% mole based upon total solvent of ammonia, in the liquid phase at a temperature from about 15 C. to about 110° C.

3. The process of claim 2 wherein the non- to tri-benzene is non- to mono-alkylbenzene wherein any alkyl is acyclic alkyl of from 1 to 4 carbon atoms.

4. The process of claim 2 wherein the alkylamine is methylamine.

5. The process of producing cyclohexenes by intimately contacting non- to tri-alkylbenzene of from 6 to 20 carbon atoms with from about 2 gram-atoms to about 10 gram-atoms per mole of said non- to tri-alkylbenzene of alkali metal of atomic number from 19 to 37, in solvent comprising from about 7 moles to about 50 moles

per mole of said non- to tri-alkylbenzene of lower alkylamine of from 1 to 4 carbon atoms and up to about 40% mole based on total solvent of ammonia, in the liquid phase at a temperature from about 15° C. to about 150° C.

6. The process of producing cyclohexenes by intimately contacting non- to mono-alkylbenzene wherein any alkyl is acyclic alkyl of from 1 to 4 carbon atoms with

from about 2 gram-atoms to about 10 gram-atoms per mole of said non- to mono-alkylbenzene of alkali metal of atomic number from 10 to 37, in solvent comprising from about 7 moles to about 50 moles per mole of said non- to mono-alkylbenzene of alkylamine of from 1 to 2 carbon atoms and up to about 25% mole based on total solvent of ammonia, the ratio of moles of said am-

monia to gram-atoms of said alkali metal not exceeding 3, in the liquid phase at a temperature from about 20° C. to about 100° C.

7. The process of claim 6 wherein the non- to mono-alkylbenzene is benzene.

8. The process of claim 6 wherein the non- to mono-alkylbenzene is toluene.

9. The process of producing cyclohexenes by intimately contacting non- to tri-alkylbenzene of from 6 to 20 carbon atoms with from 2 gram-atoms to about 10 gram-atoms per mole of said non- to tri-alkylbenzene of alkali metal of atomic number from 19 to 37, in from about 7 moles to about 50 moles per mole of said non- to tri-alkylbenzene of lower alkylamine of from 1 to 2 carbon atoms, in the liquid phase at a temperature of from about 15° C. to about 110° C.

10. The process of claim 9 wherein the non- to tri-alkylbenzene is Tetralin.

11. The process of producing cyclohexenes by intimately contacting non- to mono-alkylbenzene wherein any alkyl is acyclic alkyl of from 1 to 4 carbon atoms with from about 4 gram-atoms to about 8 gram-atoms per mole of said non- to mono-alkylbenzene of alkali metal of atomic number from 19 to 37, in from about 7 moles to about 50 moles per mole of said non- to mono-alkylbenzene of alkylamine of from 1 to 2 carbon atoms, in the liquid phase at a temperature from about 30° C. to about 80° C.

12. The process of producing cyclohexene by intimately contacting benzene with from about 4 gram-atoms to about 8 gram-atoms per mole of benzene of potassium, in from about 7 moles to about 50 moles per mole of benzene of alkylamine of from 1 to 2 carbon atoms, in the liquid phase at a temperature from about 20° C. to about 100° C.

13. The process of claim 12 wherein the alkylamine is methylamine.

14. The process of producing alkylcyclohexene by intimately contacting alkylbenzene wherein the alkyl is acyclic alkyl of from 1 to 4 carbon atoms, with from about 4 gram-atoms to about 8 gram-atoms per mole of alkylbenzene of potassium, in from about 7 moles to about 50 moles per mole of alkylbenzene of alkylamine of from 1 to 2 carbon atoms, in the liquid phase at a temperature from about 30° C. to about 80° C.

15. The process of claim 14 wherein the alkylbenzene is toluene.

16. The process of claim 14 wherein the alkylbenzene is cumene.

17. The process of claim 14 wherein the alkylamine is methylamine.

18. The process of claim 14 wherein the alkylamine is ethylamine.

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