

1

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## CYCLOHEXADIENE PRODUCTION

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This invention relates to a process for the partial reduction of aromatic compounds. More particularly, it relates to a process for the production of cyclohexadienes by partial reduction of the corresponding aromatic compounds.

Several methods are available in the art for the partial reduction of aromatic compounds, e.g., benzene. U.S. Patent No. 2,182,242, issued May 3, 1948, to Wooster, describes a low-temperature reduction of benzene by contact with sodium in liquid ammonia in the presence of added acidic materials such as water and alcohol to produce cyclohexadiene. Such a method suffers from the disadvantage that the sodium is recovered from the reaction system as the hydroxide or alkoxide, forms from which the sodium is not readily recoverable. The resulting effective loss of sodium precludes the use of such a process on a commercial basis for economic reasons. It is also known, see Benkeser, J. Am. Chem. Soc., 77, 3230 (1955), that benzene may be partially reduced by reduction with lithium in certain primary amines, such as methylamine and ethylamine, without the addition of added acidic components, but in this process the products observed are cyclohexene and cyclohexane. Practical and economically feasible methods for the partial reduction of benzene to cyclohexadiene by such procedures have not heretofore been available.

It is an object of the present invention to provide an improved process for the partial reduction of aromatic hydrocarbons. More particularly, it is an object of the present invention to provide an improved process for the partial reduction of certain mononuclear aromatic hydrocarbons to the corresponding 1,4-cyclohexadienes. A specific object is to provide a process for the partial reduction of benzene to 1,4-cyclohexadiene.

It has now been found that these objects are accomplished by the process of reacting certain mononuclear aromatic hydrocarbons with lithium in solution in liquid ammonia in the substantial absence of added acidic materials. The process of the invention results in the efficient production of cyclohexadienes, along with lesser amounts of corresponding cyclohexenes, and offers the advantage of providing lithium amide as the metal-containing product from which the elemental lithium is readily recoverable, as by pyrolysis of the lithium amide to afford elemental lithium. The utilization of lithium as the metallic reactant appears to be critical as utilization of other alkali metals, sodium for example, does not result in cyclohexadiene production.

The aromatic reactants suitably employed in the process of the invention are mononuclear aromatic hydrocarbons containing a single six-membered carbocyclic aromatic ring. Suitable aromatic hydrocarbons contain from 6 to 20 carbon atoms and comprise benzene and aliphatic hydrocarbyl-substituted benzene. Although the process of the invention is operable when the central benzene nucleus possesses a plurality of aliphatic hydrocarbyl substituents, best results are obtained when the central benzene nucleus is unsubstituted or possesses from 1 to 2 alkyl substituents of from 1 to 14 carbon atoms. Preferred aromatic reactants are therefore characterized as non- to di-alkylbenzene wherein any alkyl substituent is

2

alkyl of from 1 to 14 carbon atoms, preferably 1 to 4. Illustrative of such preferred reactants are benzene, toluene, ethylbenzene, cumene, hexylbenzene, decylbenzene, xylene, o-diethylbenzene, p-diisopropylbenzene, m-octyltoluene, and the like. Particularly preferred as the organic reactant is benzene.

The process of the invention is conducted by contacting the non- to di-alkylbenzene with lithium in liquid ammonia in the substantial absence of hydrolytic agent, that is, hydrolytic agent other than ammonia. By the term "hydrolytic agent" as employed herein is meant a substance capable of reacting with the lithium under the conditions of the reaction to liberate hydrogen. The use of ammonia substantially free of hydrolytic agent is highly desirable from a process standpoint, however the presence of small amounts of added hydrolytic agent, e.g., up to about 10-15% by weight, may be tolerated without losing the advantages of the invention, but the yield of desired product is decreased by the presence of such materials and in the preferred modification of the process of the invention, no added hydrolytic agent is employed.

The ammonia is employed in molar excess over the lithium and the aromatic reactant. Molar ratios of ammonia to the benzene from about 3:1 to about 100:1 are satisfactory, although molar ratios from about 10:1 to about 50:1 are preferred. The lithium is customarily employed in amounts in excess of the benzene reactant. The probable stoichiometry of the reaction requires utilization of two gram-atoms of lithium per mole of benzene reactant. Without wishing to be bound by any particular theory, it appears probable that the lithium reacts directly with the benzene reactant to produce a mono-metal derivative, e.g., a benzene free-radical anion, which subsequently reacts with ammonia to introduce hydrogen into the aromatic ring and form lithium amide. A subsequent additional reaction with lithium and ammonia results in the formation of the observed cyclohexadiene product. Thus, two gram-atoms of lithium are required to effect the desired conversion of each mole of benzene reactant. While it appears to be inherent in the process of the invention that some lithium will react directly with the ammonia to produce hydrogen and lithium amide and thus will not be available for utilization in the desired reduction process, amounts of lithium that are less than stoichiometric may be utilized if it is not desired to effect a high conversion of the benzene reactant. Thus, ratios of gram-atoms of lithium to moles of benzene reactant from about 0.25:1 to about 10:1 are suitably employed. Best results are obtained when the ratio of gram-atoms of lithium to moles of benzene is from about 1:1 to about 8:1 and ratios from about 2:1 to about 6:1 are particularly satisfactory.

The partial reduction process of the invention is conducted at a comparably elevated temperature and pressure and is typically effected in an autoclave or similar reaction vessel. In contrast with previously reported alkali metal-ammonia reductions which require low temperature, e.g., -40° C., the process of the invention is conducted at temperatures from about 10° C. to about 135° C., although the temperature range from about 25° C. to about 80° C. is preferred. The reaction pressure is that which is sufficient to maintain the ammonia substantially in the liquid phase during the reduction process. Pressures from about 2 atmospheres to about 300 atmospheres are suitable and frequent advantage is taken of the pressures generated when the reaction mixture is allowed to reach reaction temperature in a sealed reaction vessel. In the latter modification the reaction is conducted in an atmosphere of ammonia. The presence of other reactive gaseous ma-

terials is desirably avoided. It is, on occasion, useful to pressurize the reactor with an inert gas such as argon, helium, methane or the like, prior to or simultaneously with heating the reaction mixture to reaction temperature, although in the preferred modification of the process of the invention no such inert gas is employed.

The process of the invention is operable in the presence of inert diluents, e.g., aliphatic hydrocarbons such as hexane, heptane, 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. Subsequent to reaction the product mixture is separated and the desired cyclohexadiene product is recovered by conventional methods such as fractional distillation, selective extraction, crystallization and the like. The unreacted ammonia is recoverable for use in subsequent operations as is any unreacted benzene reactant. A principal advantage of the process of the invention lies in the fact that the lithium is recovered as the amide regardless of the mode of lithium reaction. As previously stated, when lithium amide is obtained as the reaction product, the lithium is easily recoverable, in contrast with prior processes which result in production of metal-containing products from which the metal is not readily regenerated.

The principal products of the process of the invention are cyclohexadienes, although lesser amounts of cyclohexenes are also formed. For example, from benzene is obtained 1,4-cyclohexadiene and cyclohexene. Although there exists the possibility of formation of 1,3-cyclohexadienes, as well as 1,4-cyclohexadienes, little if any of the 1,3-isomer is produced. When the benzene possesses alkyl substituent(s) position isomers of the alkyl group relative to the double bonds present in the ring are observed, e.g., from toluene is obtained a mixture of 1-methyl-1,4-cyclohexadiene and 3-methyl-1,4-cyclohexadiene, and from p-xylene is obtained a mixture of 1,4-dimethylcyclohexadiene and 3,6-dimethylcyclohexadiene.

The cyclohexadiene products are useful in a variety of applications, particularly as chemical intermediates where they serve as monomers in the formation of useful copolymers and are additionally suitable for epoxidation to form mono- and di-epoxides which are useful as precursors for epoxy resins.

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 with lithium in ammonia was effected by charging 0.10 mole of benzene, from 2.4 to 2.7 moles of liquid ammonia, and varying amounts of lithium to an autoclave. The reactor was sealed and maintained at reaction temperature for the indicated period, after which it was cooled and opened and the product mixture removed therefrom. The organic materials and ammonia were separated from the amide by distillation and the product composition was determined by gas-liquid chromatography. The results of this series are shown in Table I.

TABLE I

Lithium, G-atoms	Temp., ° C.	Time, Hours	Product, percent Yield		
			Cyclo- hexane	Cyclo- hexene	1,4-Cyclo- hexadiene
0.1-----	53	2.5	0	2.6	7.4
0.2-----	60	2	trace	5.1	30.7
0.4-----	25	12	0.5	4.4	39.6
0.4-----	60	2	0	5.2	41.6
0.8-----	60	8	0	42.2	54.5
0.4-----	100	0.5	0.2	19.1	34.8

The yields in each case are calculated on the basis of benzene charged, and the material not accounted for in the reduced products was unreacted benzene.

#### Example II

To a reactor was charged 0.1 mole of toluene, 0.4 mole of lithium and 2.6 moles of ammonia. The reactor was sealed and maintained at 60° C. for 4 hours. The reactor was cooled and opened and the ammonia and organic materials were separated from the amide by distillation. The product mixture was analyzed by gas-liquid chromatographic methods and was found to contain a 3.7% yield of methylcyclohexene and a 20.1% yield of methylcyclohexadiene, each yield being based on the toluene charged. The remaining portion of the product mixture was unreacted benzene.

We claim as our invention:

1. The process of producing a cyclohexadiene product by contacting a mononuclear aromatic hydrocarbon of from 6 to 20 carbon atoms, selected from benzene and benzene of from 1 to 2 alkyl substituents, with lithium and ammonia, in the liquid phase, in the substantial absence of hydrolytic agent other than ammonia, at a temperature from about 10° C. to about 135° C., in a reaction mixture consisting essentially of said aromatic hydrocarbon, said lithium and said ammonia.

2. The process of claim 1 wherein the aromatic hydrocarbon is toluene.

3. The process of claim 1 wherein the aromatic hydrocarbon is benzene.

4. The process of claim 1 wherein the ratio of gram-atoms of lithium to moles of said aromatic hydrocarbon is from about 1:1 to about 8:1 and the molar ratio of said ammonia to said aromatic hydrocarbon is from about 3:1 to about 100:1.

5. The process of claim 4 wherein the aromatic hydrocarbon is benzene and the temperature is from about 25° C. to about 80° C.

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