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ALKYLATION PROCESS

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ABSTRACT OF THE DISCLOSURE

An alkylatable aromatic hydrocarbon is alkylated with a saturated hydrocarbon utilizing a catalyst comprising aluminum chloride and the higher-valence halide of a metal which forms at least two metal halides differing in valence.

Description of the invention

This invention relates to a conversion process for the alkylation of alkylatable aromatic hydrocarbons into more useful compounds. More specifically, this invention is concerned with a conversion process for the alkylation of an alkylatable aromatic hydrocarbon with a saturated hydrocarbon utilizing a novel catalyst comprising aluminum chloride and the higher-valence halide of a metal which forms at least two metal halides differing in valence.

It is, therefore, an object of this invention to provide a process for the alkylation of alkylatable aromatic hydrocarbons utilizing a novel alkylation catalyst.

A specific object of this invention is to provide a novel method and a novel catalyst for alkylating alkylatable aromatic hydrocarbons to provide the desired alkylated product in high yields.

One embodiment of the invention relates to a process for the alkylation of an alkylatable aromatic hydrocarbon with a saturated hydrocarbon at alkylation conditions in the presence of a catalyst comprising aluminum chloride and the higher-valence halide of a metal which forms at least two metal halides differing in valence.

A second embodiment of this invention relates to a process for the alkylation of an alkylatable benzene hydrocarbon with a saturated hydrocarbon at alkylation conditions including a temperature in the range of about 0° to about 200° C. and a pressure in the range of from about atmospheric to about 200 atmospheres in the presence of a catalyst comprising aluminum chloride and the higher-valence halide of a metal which forms at least two metal halides differing in valence.

The process of my invention is applicable to the alkylatable aromatic hydrocarbons including, for example, benzene, toluene, ortho-xylene, meta-xylene, para-xylene, ethylbenzene, ortho-ethyltoluene, meta-ethyltoluene, para-ethyltoluene, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, diethylbenzene, triethylbenzene, normal propylbenzene, isopropylbenzene, etc., and mixtures thereof. Preferred alkylatable aromatic hydrocarbons are benzene and monoalkylated benzenes. Higher molecular weight alkyl aromatic hydrocarbons are suitable. These include those aromatic hydrocarbons such as are produced by the alkylation of aromatic hydrocarbons with olefin polymers and are used as intermediates in the preparation of sulfonate surface-active agents. Such products include hexylbenzenes, nonylbenzene, dodecylbenzenes, pentadecylbenzenes, hexyltoluenes, nonyltoluenes, dodecyltoluenes, pentadecyltoluenes, etc. Very often, the product is obtained as a high boiling fraction in which the alkyl group attached to the aromatic nucleus varies in size from about C_9 to C_{18}. Other suitable aromatic hydrocarbons, which at specified conditions, depending upon

the melting point of the aromatic chosen, would be in liquid form, would include those aromatic hydrocarbons with two or more aryl groups such as diphenyl, diphenylmethane, triphenyl, triphenylmethane, fluorene, stilbene, etc. Examples of other aromatic hydrocarbons utilizable in the scope of this invention which, because they may be normally solid at the alkylation conditions, are alkylated in a solvent, preferably an excess of the saturated hydrocarbon, include those containing condensed aromatic rings. These include naphthalenes, alkylnaphthalenes, anthracene, phenanthrene, naphthacene, rubrene, etc. Of the above-mentioned aromatic hydrocarbons that could be utilized in the process of this invention, the benzene hydrocarbons are preferred, and of the preferred benzene hydrocarbons, benzene itself is particularly preferred.

The saturated hydrocarbons, acting as the alkylating agent, may be selected from diverse materials including the acyclic paraffin hydrocarbons and cycloparaffin hydrocarbons are the alkanes and cycloalkanes containing tertiary carbon atoms. Other suitable alkylating agents include normal butane, normal pentane, isopentane, normal hexane, isohexane, normal heptane, 2-methylhexane, normal octane, etc. Suitable cycloalkanes such as the cyclopentanes and cyclohexanes, including cyclopentane, methylcyclopentane, dimethylcyclopentanes, cyclohexane, methylcyclohexane, dimethylcyclohexanes, etc. Mixtures of saturated hydrocarbons may also be utilized.

As hereinabove set forth, the invention is concerned with a process for the alkylation of alkylatable aromatic hydrocarbons, said process being effected by the presence of a catalyst which possesses a high degree of hydrocarbon conversion activity and is particularly effective as an alkylation catalyst for alkylatable aromatic hydrocarbons. The catalyst comprises aluminum chloride and a higher-valence halide of a metal which forms at least two metal halides differing in valence. Suitable metals which form at least two metal halides differing in valence include copper, mercury, iron, tin, cobalt, molybdenum, manganese, and chromium. The various bromides and chlorides of the above metals including mercuric chloride, mercuric bromide, cupric chloride, cupric bromide, ferric chloride, ferric bromide, stannic chloride, stannic bromide, cobaltic chloride, cobaltic bromide, molybdenum trichloride, molybdenum tetrachloride, molybdenum tetrabromide, molybdenum pentabromide, manganese trichloride, manganese tribromide, chromic chloride, chromic bromide, etc., are thus utilizable in the scope of my invention.

A particularly preferred catalyst for use in the process of this invention is the catalyst comprising aluminum chloride and cupric chloride. The aluminum chloride may be used in a catalytic amount, or preferably, in equimolar amounts with the cupric chloride. The chlorides may be added separately or as a complex, $Al_3Cl_3 \cdot CuCl_2$.

The process of this invention utilizing the catalyst hereinbefore set forth may be effected in any suitable manner and may comprise either a batch or a continuous type operation. The preferred method by which the process of this invention may be effected is a continuous type operation. One particular method is the operation in which the alkylatable aromatic hydrocarbon and the saturated hydrocarbon are continuously charged to a reaction zone containing the desired catalyst, said zone being maintained at the proper operating conditions of temperature and pressure, that is, a temperature in the range of from about 0° to about 200° C. and preferably a temperature of from about 20° to about 100° C., and a pressure including a pressure of from about atmospheric to about 200 atmospheres or more. The rate at which the hydrocarbon charge is added may be varied within a relatively wide range. The reaction zone may comprise an unpacked vessel or coil or may contain a packing material. The two reactants may be charged through separate lines, or, if so desired, may be admixed prior to entry into said reaction zone and charged thereto in a single stream. This charge passes into the reaction zone containing the catalyst in an upward, downward, or radial flow and the alkylated product is continuously withdrawn, separated from the reactor effluent and recovered, while any other unreacted starting material may be recycled to form a portion of the feed stock. Another continuous type operation comprises the moving bed type in which the reactants and the catalyst move either concurrently or countercurrently to each other while passing through said reaction zone.

Still another type operation which may be used in the batch type operation in which a quantity of the alkylatable aromatic hydrocarbon, the saturated hydrocarbon and the catalyst are placed in an appropriate apparatus such as, for example, a rotating or stirred autoclave. The apparatus is then maintained at the desired temperature for a predetermined residence time at the end of which time the flask and contents thereof are cooled to room temperature (if a higher reaction was employed) and the desired reaction product is recovered by conventional means, such as, for example, by washing, drying, fractional distillation, crystallization, etc.

The following examples are introduced for the purpose of illustration only with no intention of unduly limiting the broad scope of the present invention.

Example I

In this example, 20 grams (0.2 mole) of benzene and 24 grams (0.33 mole) of isopentane were stirred and mixed at room temperature with 22 grams of catalyst comprising approximately equimolar amounts of aluminum chloride and cupric chloride. At the end of about 30 minutes, the product was washed with ice water. The benzene-soluble material was separated and analyzed by Preparative Gas Liquid Chromatography (Prep. GLC). A mixture of pentylbenzenes including neopentylbenzenes, t-pentylbenzene and sec-isopentylbenzene (i.e. 2-phenyl-3-methylbutane) was obtained. Byproducts of the reaction included ethylbenzene, isopropylbenzene and 1,1-diphenylethane.

Example II

In this example, 46.5 grams (0.5 mole) of toluene and 53 grams (0.62 mole) of 2,3-dimethylbutane were mixed and stirred at 25–27° C. with a catalyst comprising aluminum chloride and cupric chloride. The vigorous evolution of HCl was noted. The product was subsequently treated with ice water followed by ether extraction and a product containing two hexylbenzene isomers including 2-phenyl-2,3-dimethylbutane and 2-phenyl-3,3-dimethylbutane was recovered.

I claim as my invention:

1. A process for the alkylation of an alkylatable aromatic hydrocarbon with a saturated hydrocarbon at alkylation conditions in the presence of a catalyst comprising aluminum chloride and a higher-valence halide of a metal which forms at least two metal halides differing in valence.

2. The process of claim **1** further characterized in that said alkylatable aromatic hydrocarbon is a benzene hydrocarbon.

3. The process of claim **1** further characterized in that said saturated hydrocarbon is an acyclic paraffin hydrocarbon.

4. The process of claim **1** further characterized in that said saturated hydrocarbon is a cycloparaffin hydrocarbon.

5. The process of claim **1** further characterized in that said alkylation conditions include a temperature in the range of from about 0° to about 200° C. and a pressure in the range of from about atmospheric to about 200 atmospheres.

6. The process of claim **1** further characterized in that said metal which forms at least two metal halides differing in valence is copper and that said halide of the metal is chloride.

7. The process of claim **6** further characterized in that said benzene hydrocarbon is benzene and that said saturated hydrocarbon is isopentane.

8. The process of claim **6** further characterized in that said benzene hydrocarbon is toluene and that said saturated hydrocarbon is 2,3-dimethylbutane.

References Cited

UNITED STATES PATENTS

2,304,290	12/1942	Van Peski	260—671
2,426,665	9/1947	Bloch	260—671
2,433,020	12/1947	Becker	260—671
3,109,038	10/1963	Myers	260—671

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