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PRODUCTION OF ALKENYL AROMATICS

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This invention relates to derivatives of aromatic compounds. In one modification it relates to alkenyl derivatives of aromatic compounds. In another modification it relates to normal alkyl derivatives of aromatic compounds. As specific modifications it relates to the alkenylation of aromatic hydrocarbons and to the production of normal alkyl derivatives of aromatic hydrocarbons.

Normal alkenyl aromatic compounds and normal alkyl aromatic compounds are valuable intermediate compounds both in their own rights and as intermediates in organic syntheses. They may be used for the production of normal aliphatic derivatives of such compounds as aminobenzenes, aminonaphthalenes, phenols, naphthols, aminophenols, aminonaphthols, quinolines, and the like. These materials can be used in the preparation of oxidation inhibitors, pharmaceuticals, dyestuffs, and explosives. The development of the full potentialities of normal aliphatic derivatives of such compounds has been precluded by the absence of suitable sources of such compounds. Thus, when olefins are used to alkylate aromatic compounds the normal alkyl derivative is produced only in the case of ethylene and with other olefins it is impossible to produce a normal alkyl derivative by catalytic alkylation. Synthetic methods for the production of normal alkyl derivatives have been limited heretofore to reactions of the Wurtz-Fittig type in which aromatic halides have been condensed, in the presence of a metal such as sodium, with normal alkyl halides. The best yields reported for such reactions have not exceeded about 30 per cent of the theoretical yield and more often actual yields are from about 10 to 20 per cent of the theoretical yields. Other disadvantages of such synthesis operations include the use of large quantities of metals such as sodium with appreciable attendant hazards, the employment of expensive intermediate compounds, the necessity of special solvents, and the relatively difficult production of normal alkyl halides.

An object of this invention is to produce normal aliphatic derivatives of aromatic compounds.

Another object of this invention is to produce normal alkyl derivatives of aromatic compounds.

A further object of this invention is to produce normal alkenyl derivatives of aromatic compounds.

A still further object of this invention is to react low-boiling aromatic hydrocarbons with low-boiling normal 1,3-diolefins to produce normal monoalkenyl derivatives of said aromatic hydrocarbons.

Still another object of this invention is to produce normal butyl benzene.

Further objects and advantages of my invention will become apparent to one skilled in the art from the accompanying disclosure and discussion.

I have now found that aromatic compounds, including aromatic hydrocarbons, phenols, naphthols, and aromatic halides, can be reacted with normal 1,3-diolefins to produce alkenyl derivatives of said aromatic compounds. I have further found that such alkenyl derivatives include normal monoalkenyl derivatives which can be successfully subjected to nondestructive hydrogenation to produce the corresponding normal alkyl derivatives. I have further discovered that such derivatives can be produced in extremely high yields and can be recovered in substantial quantities in a condition of high purity. As the aromatic reactant of my process I prefer to use benzene, naphthalene, simple alkyl derivatives of these hydrocarbons such as toluene, ethylbenzene, xylenes, and the like, phenol, naphthols, and simple alkyl derivatives of these materials, and aromatic halides such as phenyl chloride, phenyl bromide, one of the naphthyl chlorides, and the like, although other alkenylatable aromatic compounds are not to be excluded from the broad concept of my invention. As the diolefin reactant I prefer to use a low-boiling normal 1,3-diolefin such as 1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, and the like. Although it is a primary object of my invention to produce normal aliphatic derivatives by the use of normal 1,3-diolefins, it is to be understood that alkyl derivatives of normal 1,3-diolefins, such as 5-methyl-1,3-hexadiene and 6-methyl-1,3-heptadiene, to produce aromatic derivatives such as 1-phenyl-5-methyl hexylene and 1-phenyl-6-methyl heptylene, and the like, are not to be excluded from the broad concepts of my invention.

Broad features of this process may be more readily understood by considering a typical procedure. A blend of butadiene in benzene, in which the benzene is present in substantial molar excess, serves as the primary feed stock. The blend is charged to a reaction zone at moderate temperatures and pressures where it is intimately commingled with a liquid complex compound of boron trifluoride such as those to be hereinafter described. The effluent is preferably continuously removed from the reaction zone and after mechanical separation of the catalyst phase, the hydrocarbon stream is washed free of dissolved boron fluoride and the excess benzene is recovered by fractional distillation. The debenzenized product is further fractionally distilled to separate a main product (normal butenyl benzene, or phenyl butene) boiling at about 365 to about 370° F., and a higher-boiling kettle product. The main product fraction may be hydrogenated over a conventional hydrogenation catalyst such as Raney nickel, platinum or any of the more rugged industrial hydrogenation catalysts to yield n-butylbenzene, which ordinarily requires no further purification.

I have found that efficient catalysts for such alkenylation reactions can be prepared by substantially saturating with a boron trihalide an organic carboxylic acid. A preferred boron trihalide is boron trifluoride although I do not intend to exclude other boron trihalides, particularly boron trichloride and boron tribromide which are low-boiling materials. Because they are obtainable readily and at low prices, I prefer to use aliphatic monocarboxylic acids having not more than about five carbon atoms per molecule, particularly those which are saturated. Among the saturated aliphatic acids I intend to include in addition to the series formic, acetic, propionic, etc., also various substituted acids, such as the well known chloroacetic acids, and bromoacetic acids, cycloalkyl and aryl substituted derivatives, such as benzoic acid, hexahydrobenzoic acid, various toluic acids, naphthoic acids, naphthenic acids, and the like, and hydroxyacids such as glycollic acid, lactic acid, hydracrylic acid, etc. These later acids generally require about twice as much boron trihalide to produce a saturated complex as do the other monocarboxylic acids. Some dicarboxylic acids, such as oxalic acid and malonic acid, may also be used.

The complex catalyst for the alkenylation reaction is preferably prepared by adding the boron trihalide to the acid or to a suitable aqueous solution thereof until the acid has become substantially completely saturated with the boron trihalide. Although essentially pure compounds can be prepared, in actual practice the acids appear to have taken up from about 0.5 to about 1 mol of boron trihalide per mol of acid when they are completely saturated. Accordingly the catalyst used in accordance with the present invenvention is formed by the combination of from about 0.5 to about 1 mol of boron trihalide with 1 mol of acid. These addition compounds are stable at ordinary temperatures and under the reaction conditions used for the alkenylation. The reaction which takes place when the catalyst is formed is exothermic and the rate of addition of boron trihalide should be controlled together with the cooling of the reacting mixture to avoid reaction temperatures above about 200° F. This catalyst preparation reaction may be conducted, if desired, under pressure, particularly when using boron trifluoride or boron trichloride. Saturation of the acid will be noted by lack of additional reaction upon the continued addition of boron trihalide. The exact mechanism of the addition reaction and the formulae of the compounds formed in the preparation of the catalyst have not been determined with certainty. One reaction is the formation of a complex between the boron trihalide and the carboxylic acid, and another reaction is the formation of a complex between the boron trihalide and any water which may be present. In those instances in which the carboxylic acid is solid at the temperature desired for the catalyst preparation, it may be treated in finely divided form or in liquid form by dissolving it in a small amount of water or in some other solvent such as an alcohol or an ether. Such solvents also form complexes with boron trihalides which, however, do not detract from the catalytic action of the desired boron trihalide-carboxylic acid complex. When an active catalyst of my preferred composition loses appreciable amounts of boron trihalide during use, its activity decreases and for this reason it is desirable to add during a continuous process small amounts of the boron trihalide initially used to prepare the catalyst, continuously or intermittently, in order that the activity of the catalyst will remain, or be maintained, substantially constant.

Many of the catalysts are liquid materials at the usual reaction temperatures and have viscosities sufficiently low that intimate mixing during the alkenylation reaction with the reacting mixture can be effected without too great difficulty. These materials can be employed as such, preferably with intimate mixing, with the reaction mixture. If it is desired to use such a catalyst in the solid form it may be used in admixture with porous granular catalyst supports such as activated charcoal, activated alumina, activated bauxite, and the like, although when using boron trifluoride-containing complexes it is preferable not to use a granular material containing appreciable amounts of silica.

In the alkenylation step the reaction appears to be primarily monoalkenylation to form monoalkenyl derivatives of the aromatic compound. It also appears that secondary reactions take place to certain extents, including cyclization and/or polymerization of the resulting monoalkenyl derivatives. This conclusion is based on the observation that the aromatic compound reacted is molecularly equivalent to the diolefin reacted. If extensive polyalkenylation occurred, to form di- or tri-alkenyl aromatic derivatives, the amount of aromatic hydrocarbon reaction would be substantially less than the molecular equivalent of the diolefin, while if the monoalkenyl derivative entered into reaction with the aromatic hydrocarbon, to form the corresponding di-substituted paraffin hydrocarbon, the amount of aromatic hydrocarbon reacted would be substantially greater than a molecular equivalent of the diolefin. No appreciable polymerization of the diolefin is believed to take place under preferred conditions of operation, a conclusion deduced from a consideration of the relative amounts of reactants which undergo reaction and from the characteristics of such high-boiling products. Such results contrast with the results obtained when catalysts such as sulfuric acid are used with the same reactants. Thus, when benzene and 1,3-butadiene are reacted in the presence of sulfuric acid it has been reported that the product is diphenyl butane and that no phenylbutene is produced.

In order to favor the desired primary reaction I prefer to use moderate reaction temperatures, relatively short reaction periods, and relatively high molar ratios of aromatic compound to diolefin reactant. The reaction may be satisfactorily and conveniently conducted at a temperature between about 75 and about 150° F., with a temperature between about 80 to 90° F. and about 110 to 120° F. being preferred. Temperatures above 150° F., or below 75° F., are not to be excluded, however. The average reaction time may be between a few minutes and a few hours, with satisfactory results being obtained with a reaction time between about 5 and about 20 minutes. The molar ratio of aromatic compounds to diolefin in the feed to a continuous reaction step may be between about 2:1 and about 10:1 with satisfactory operation generally being obtained with a a ratio between about 4:1 and about 6:1. Intimate mixing of the reaction mixture, accompanied by recirculation, will generally result in higher effective ratios in the reaction zone. In some instances it is desirable to use moderate superatmospheric pressures, particularly with the lower boiling reactants, but generally the pressure need not be appreciably above that which will insure that the reactants are present in liquid phase and to insure that the catalyst is adequately saturated with the boron trihalide. As previously stated, it is preferred that the reacting mixture and the catalyst be intimately admixed. This may be accomplished by efficient stirring mechanism, by continuously recirculating in a closed cycle a substantial amount of the reaction mixture comprising reactants, products and catalyst, by pumping such a reaction mixture through a long tube coil at a rate such that conditions of turbulent flow exist, or by other means well known to those skilled in the art of hydrocarbon alkylations. It is preferred that the reaction mixture contain at least about 5 per cent by volume of the catalyst and that the amount of catalyst present should not exceed that which will permit a continuous phase of reacting materials when the reaction mixture is intimately admixed. Thus it is desired that the catalyst phase not be the continuous phase when a liquid catalyst is used. Inert materials may be present during the reaction, such as relatively nonreactive impurities normally accompanying the reactants, added low-boiling paraffin hydrocarbons such as a paraffinic naphtha fraction, or the like.

When 1,3-butadiene is the diolefin reactant the monoalkenyl product is substantially completely the normal alkenyl derivative. With diolefin reactants containing a higher number of carbon atoms per molecule such high yields of the normal derivative will often not be obtained but it will still be possible to obtain quite substantial yields of the normal alkenyl derivative. In any case a fraction containing, or comprising essentially, the desired normal alkenyl derivative may be readily separated from the reaction effluents, generally by passing the effluents to a settling chamber wherein the catalyst separates from a liquid phase containing unreacted charge stock and reaction products, and separating from this liquid phase, as by fractional distillation, a fraction of any desired purity.

As will be appreciated the normal alkenyl derivative may, in many instances, be a desired product of the process. However, I have found that this material may be readily converted to the normal alkyl derivative by nondestructive hydrogenation. This hydrogenation will most often be conducted in a manner such that the alkenyl group is saturated by hydrogen. However, it will be appreciated that, particularly when aromatic hydrocarbons are reacted in accordance with my invention, not only may normal alkyl derivatives thereof be produced by such a nondestructive hydrogenation, but the hydrogenation may be extended to include partial or complete saturation of the aromatic nucleus. Thus, it is possible to react a benzene with a low-boiling 1,3-diolefin to produce a normal alkenyl derivative of said benzene, and subsequently to hydrogenate this product, in one or more steps, to produce a normal alkyl derivative or a corresponding normal alkyl cyclohexane. Likewise, a naphthalene may be converted to a normal alkenyl derivative, and this product may subsequently be hydrogenated, in one or more steps, to produce a normal alkyl derivative, a normal alkyl tetralin, or a normal alkyl decalin. For such hydrogenations any suitable known nondestructive hydrogenation catalyst may be employed which is capable of effecting saturation of the alkenyl group without saturation of the aromatic nucleus or without reaction of any other reactive group in the alkenyl compound. So-called "Raney nickel" has been found desirable in accomplishing this result when the hydrogenation is conducted at moderate temperatures and pressures. More drastic hydrogenation conditions will be necessary in order to produce the more saturated products just discussed.

Thus, in the selective hydrogenation of the olefinic linkage, the rate of absorption of hydrogen may amount to about 1 mol per hour at pressure of 20 to 50 pounds per square inch and temperatures ranging from about 75° F. to about 150° F. Nuclear hydrogenation can be effected with the same catalyst at pressures of about 500 to 5000 pounds per square inch and at temperatures of about 250 to 350° F.

The following examples illustrate my invention further. However, it is to be understood that specific limitations expressed in such examples are not to be used to restrict my invention unduly.

Example I

The alkenylation of benzene with butadiene was carried out in a packed column at substantially atmospheric pressure using a boron fluoride-acetic acid complex ($CH_3COOH.BF_3$) as the catalyst. The liquid addition compound was suspended on activated charcoal. Benzene was added at the top of the column and gaseous butadiene was introduced at the bottom. The total effluent was removed from a small reservoir at the bottom of the reactor. The mol ratio of benzene to butadiene in this run was equivalent to 8.5:1.0 and the temperature was held at 80 to 90° F. n-Butenylbenzene distilling at 158–162° F. at 12 mm. pressure amounted to 63 per cent by weight of the total debenzenized product. This fraction was converted quantitatively to n-butylbenzene by hydrogenation over Raney nickel catalyst.

Example II

Operating under conditions similar to those given in Example I, toluene may be reacted with piperylene (1,3-pentadiene) to produce n-pentenyltoluene. In this instance, the toluene-free product is subjected to a preliminary fractionation under 10 mm. pressure to effect a rough separation of higher-boiling products from the pentenyltoluene. Final purification involves fractional distillation at atmospheric pressure to give a product boiling at about 430 to 440° F. amounting to about 60 per cent of the total alkenylate. Analytical data and oxidation reactions indicate this material to be essentially 1-(p-tolyl)-2-pentene. Nondestructive hydrogenation results in quantitative reductions to 1-methyl-4-n-pentylbenzene having substantially the same boiling range as the original alkenyl derivative.

Example III

A catalyst was prepared by saturating technical butyric acid with boron trifluoride while maintaining the reaction temperature between 80 and 100° F. Approximately 0.7 mol of boron fluoride was absorbed per mol of acid.

When this catalyst is used to react benzene and 1,3-butadiene under the conditions used in Example I, a similar yield of normal butenyl benzene is obtained.

Although I have described my invention in considerable detail, with the inclusion of certain specific embodiments, it is not intended that the scope of the invention be limited unduly by such details.

I claim:

1. A process for the produtcion of an aliphatic derivative of an aromatic compound, which comprises reacting an alkenylatable aromatic compound with an open chain 1,3-diolefin in the presence of a complex catalyst resulting from substantially saturating with a boron trihalide an organic carboxylic acid, said reaction being conducted at a reaction temperature such that the major portion of the resulting reaction products are an alkenyl derivative of said aromatic compound and reaction products comprising polymers of said alkenyl derivative, polymers of said diolefin, and compounds resulting from reaction of two molecules of said aromatic compound with one molecule of said diolefin are together no more than a minor portion of said resulting reaction products, and recovering from effluents of said reaction a fraction comprising an alkenyl derivative of said aromatic compound so produced.

2. The process of claim 1 in which said catalyst is produced by substantially saturating acetic acid with boron trifluoride.

3. The process of claim 1 in which said catalyst is produced by substantially saturating with boron trifluoride an aliphatic monocarboxylic acid.

4. The process of claim 1 in which said catalyst is produced by substantially saturating with boron trifluoride a saturated aliphatic monocarboxylic acid having not more than five carbon atoms per molecule.

5. A process for the alkenylation of an aromatic hydrocarbon, which comprises reacting a low-boiling open chain 1,3-diolefin hydrocarbon with a molar excess of an alkenylatable aromatic hydrocarbon in the presence of a catalyst resulting from saturating acetic acid with boron trifluoride, said reaction being conducted at a reaction temperature such that the major portion of the resulting reaction products are an alkenyl derivative of said aromatic compound and reaction products comprising polymers of said alkenyl derivative, polymers of said diolefin, and compounds resulting from reaction of two molecules of said aromatic compound with one molecule of said diolefin are together no more than a minor portion of said resulting reaction products, and recovering from effluents of said reaction a fraction comprising an alkenyl derivative of said aromatic compound so produced.

6. The process of claim 5 wherein said diolefin is 1,3-butadiene.

7. The process of claim 5 wherein said diolefin is 1,3-pentadiene.

8. The process of claim 5 wherein said aromatic hydrocarbon is naphthalene and said diolefin is 1,3 butadiene.

9. A process for the alkenylation of an aromatic hydrocarbon, which comprises reacting a low-boiling normal 1,3-diolefin hydrocarbon with a molar excess of an alkenylatable aromatic hydrocarbon at a temperature of about 75 to about 150° F. and under sufficient pressure to maintain the reactants in the liquid phase in the presence of a catalyst resulting from saturating an organic carboxylic acid with a boron trihalide.

10. A process for the production of normal alkenyl aromatic hydrocarbons, which comprises reacting an aromatic hydrocarbon with a normal 1,3-diolefin at a reaction temperature between about 75 and about 150° F. and under a pressure sufficient to maintain the reactants in the liquid phase, said aromatic hydrocarbon and said diolefin being in a ratio of about 2:1 to 10:1 of aromatic hydrocarbon to diolefin, in the presence of a catalyst comprising a liquid complex resulting from saturating an organic carboxylic acid with a boron trihalide, and maintaining a reaction time between about 5 and about 20 minutes.

11. The process of claim 10 in which said aromatic hydrocarbon is benzene and said diolefin is 1,3-butadiene and said alkenyl aromatic hydrocarbon is butenylbenzene.

12. A process for the alkenylation of benzene with a butadiene to produce a phenylbutene, which comprises intimately contacting a hydrocarbon mixture comprising a major proportion of benzene and a minor proportion of 1,3-butadiene with an alkenylation catalyst comprising an organic carboxylic acid-boron trihalide complex containing from about 1.0 to about 2 mols of acid per mol of boron trihalide while maintaining a reaction temperature within the range of from about 75 to about 150° F. and a reaction pressure, and recovering from effluents of said reaction as a product of the process a hydrocarbon fraction which consists mainly of a phenylbutene.

13. A process for the alkenylation of an alkenylatable aromatic compound, which comprises reacting a low-boiling open chain 1,3-diolefin hydrocarbon with a molar excess of an alkenylatable aromatic compound at a temperature of about 75 to about 150° F. and under sufficient pressure to maintain the reactants in the liquid phase in the presence of a catalyst resulting from saturating an organic carboxylic acid with a boron trihalide.

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