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PRODUCTION OF AROMATIC DERIVATIVES

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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. This application is a continuation-in-part of my copending application Serial No. 433,192, filed March 3, 1942.

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.

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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-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 fluoride such as those to be hereinafter described. The effluent is preferably continuously removed from the reaction zone and after me-

chanical 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 water with a boron trihalide. 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. A preferred catalyst for use in my process is conveniently prepared by passing gaseous boron fluoride into water until the desired hydrate concentration is realized. The resulting hydrate is a liquid of relatively high specific gravity and substantially immiscible with hydrocarbons. During this reaction considerable heat is evolved and suitable means for cooling should be provided. Since the specific gravity of a completely saturated solution is approximately 1.77, convenient control of concentration can be effected by means of hydrometer determinations. Means for mechanical agitation of the absorbent liquid may be used, and I have found that such means are often helpful in obtaining some of the higher concentrations of the hydrate used in the process. In the preparation of the catalyst, the gaseous boron fluoride may be passed into water while the temperature is maintained below 150° F., and preferably above 75° F., until the water is saturated and boron fluoride passes through unabsorbed. At this point a water-boron fluoride mol ratio of approximately 1:1 is ordinarily obtained. The catalyst may be used in this form, or water may be added until a desired higher mol ratio is obtained; alternately, the addition of boron fluoride may be halted at the desired hydrate concentration by determination of the increase in weight or specific gravity of the liquid. Preferably, the alkenylation catalyst of this invention comprises a hydrated boron fluoride containing from about 1.0 to about 1.5 mols of water per mol of boron fluoride. This catalyst preparation reaction may be conducted, if desired, under pressure, particularly when using boron trifluoride or boron trichloride. When an active catalyst of this invention loses appreciable quantities of boron trifluoride or other boron trihalide during use, its activity decreases and for this reason it is desirable to add during a continuous process small amounts of 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. In most instances the resulting active catalytic material is a liquid and can be readily 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 mono-alkenylation 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 reacted 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 diphenylbutane 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 70 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 70° 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 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 pressures of 20 to 50 pounds per square inch and temperatures ranging from about 75 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

50 cc. of catalyst of composition comprising 1.5 mols of water to one mol of boron fluoride was suspended in 312 grams of benzene by agitation. Butadiene was introduced at a flow rate of 15 grams per hour until 150 grams had been absorbed. The reaction was carried out at 89 to 95° F. The alkylate was processed as above and the benzene-free alkylate was fractionated to yield 300 grams (85% yield) of phenyl-butenes boiling between 356 to 365° F. (uncorr.).

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 430–440° F. amouning 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.

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 production of normal aliphatic derivatives of aromatic compounds, which comprises reacting an aromatic compound with a normal 1,3-diolefin in the presence of a complex catalyst resulting from substantially saturating water with a boron trihalide.

2. A process for the production of normal alkyl derivatives of aromatic compounds, which comprises reacting an aromatic compound with a normal 1,3-diolefin in the presence of a complex catalyst resulting from substantially saturating water with a boron trihalide to form a normal alkenyl derivative of said aromatic compound, separating from effluents of said alkenylation a fraction comprising said normal alkenyl derivative, and subjecting said fraction to nondestructive hydrogenation to form a normal alkyl derivative of said aromatic compound.

3. 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 under alkenylation conditions in the presence of a catalyst resulting from saturating water with boron trifluoride.

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

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

6. A process for the production of a normal alkyl benzene, which comprises reacting a mixture comprising a low-boiling normal 1,3-diolefin and a molar excess of benzene under alkenyla-

tion conditions in the presence of a catalyst resulting from saturating water with boron trifluoride to produce a normal monoalkenyl derivative of benzene, separating from effluents of said alkenylation a fraction comprising said normal monoalkenyl derivative, and subjecting said fraction to nondestructive hydrogenation under conditions such that substantially only said alkenyl group is saturated with hydrogen.

7. The process of claim 6 wherein said diolefin is 1,3-butadiene and normal butylbenzene is produced.

8. The process of claim 6 wherein said diolefin is 1,3-pentadiene and normal pentylbenzene is produced.

9. A process for the production of an aryl butene, which comprises reacting an alkenylatable aromatic hydrocarbon with 1,3-butadiene at a reaction temperature not greater than about 120° F., and with a substantial molar excess of said aromatic hydrocarbon, in the presence, as a catalyst, of a complex resulting from reacting boron fluoride with about 1 to about 1.5 molar equivalents of water.

10. 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 70 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 water with boron trifluoride.

11. A process for the production of normal

alkenyl aromatic hydrocarbon, which comprises reacting an aromatic hydrocarbon with a normal 1,3-diolefin at a reaction temperature between about 70 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 water with boron trifluoride, and maintaining a reaction time between about 5 and to about 20 minutes.

12. A process for the production of a normal alkyl aromatic hydrocarbon, which comprises reacting an aromatic hydrocarbon with a normal 1,3-diolefin at a reaction temperature between about 70 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 water with boron trifluoride, maintaining a reaction time between about 5 and about 20 minutes whereby to form an alkenyl aromatic hydrocarbon, and non-destructively hydrogenating said alkenyl aromatic hydrocarbon to a normal alkyl aromatic hydrocarbon in the presence of a nickel hydrogenation catalyst at a pressure of about 20 to about 50 pounds per square inch and a temperature between about 75 and about 150° F.

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