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PRODUCTION OF ALKENYL AROMATIC COMPOUNDS

William N. Axe, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

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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 for 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.

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, naph-

thols, 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 fluoride 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 rug-

ged 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 an alcohol, preferably a monohydric aliphatic alcohol, with a boron trihalide. A preferred 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. Preferably the alcohol is one containing not more than about six carbon atoms per molecule and advantageous results are obtained when the catalyst is prepared from an aliphatic monohydric alcohol corresponding in number of carbon atoms and in molecular structure to the diolefinic reactant as is more completely disclosed and claimed in copending application Serial No. 429,698, filed February 5, 1942, of which I am a coinventor. The alkenylation catalyst is conveniently prepared by passing the boron trihalide into the alcohol at a moderate, near atmospheric temperature and pressure until absorption of the boron trihalide is complete. With alcohols containing four or more carbon atoms per molecule, and more especially with secondary and/or tertiary alcohols, side reactions may take place to produce oily polymers which are believed to be olefin polymers. Such polymers may be removed in any suitable manner, as by layer separation and/or distillation or the like. Although such side reactions reduce the yield of catalyst somewhat, compounds of excellent and specific catalytic activity are obtained from such alcohols. During the course of preparing the catalyst an exothermic reaction appears to take place, and it is generally desirable to cool this reacting mixture to prevent excessive temperature rise. The catalyst is preferably prepared at a temperature not greater than about 150° F., and generally a temperature between about 75 and 95° F. produces improved results. Completion of the catalyst-forming reaction is indicated by a cessation of heat development and also by the presence of free boron trihalide. This catalyst preparation may be conducted, if desired, under pressure, particularly when using boron trifluoride or boron trichloride. As was indicated in the aforesaid copending application, in most instances the reaction is completed with the absorption of one mol of boron fluoride per mol of alcohol. For example, in the preparation of a *sec*-butyl alcohol-boron fluoride catalyst one mol of alcohol absorbs approximately one mol of boron fluoride. Similarly, an isopropyl alcohol-boron fluoride catalyst was prepared by saturating isopropyl alcohol cooled in an ice bath with anhydrous boron fluoride. At the end of the catalyst preparation reaction, essentially one mol of boron fluoride had been absorbed per mol of alcohol. When the catalyst is subsequently used in the alkenylation reaction it tends to lose appreciable quantities of the boron trihalide during use, this loss being accompanied by a decrease in activity. 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. 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 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 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 75 and about 150° F., with a temperature between about 80 to 90 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 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 non-reactive 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 negative 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 tempera-

tures 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

To a mechanically agitated emulsion of 10 ml. of $\text{CH}_3\text{OH}\cdot\text{BF}_3$ catalyst in 150 ml. of benzene, at atmospheric pressure, gaseous butadiene was added at a rate of 5.1 gaseous liters per hour until 49.2 g. of the diolefin had been charged. The temperature of the reaction mixture was maintained at 75–85° F. The hydrocarbon was separated mechanically from the catalyst phase and the product layer was washed and dried. The product phase was then fractionally distilled at atmospheric pressure to yield a butenylbenzene cut boiling at 366–369° F. which amounted to 52 weight per cent of the total debenzenized product. The amount of unreacted benzene recovered indicated that 71.4 g. of benzene was consumed while the required amount of benzene for equimolecular union with butadiene was calculated to be 71.0 g.

Reduction of the butenylbenzene fraction was carried out as a batch operation under a hydrogen pressure of 15–50 p. s. i. g. and in the presence of Raney nickel catalyst. The saturated n-butylbenzene was identified by its boiling range of 359–360° F. and by its refractive index, N_D^{20} 1.4889.

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. 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 reduction 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 alkenyl aromatic hydrocarbons, which comprises reacting an aromatic hydrocarbon with a normal 1,3-diolefin at a reaction temperature between about 80 and about 120° F. and under a pressure sufficient to maintain the reactants in the liquid phase, said aromatic hydrocarbon and said diolefin being in a molar ratio of about 4:1 to 6:1 of aromatic hydrocarbon to diolefin, in the presence of a catalyst comprising a liquid complex containing equimolar quantities of a monohydric aliphatic alcohol and a boron trihalide and resulting from saturating a monohydric aliphatic alcohol with a boron trihalide, and maintaining

a reaction time between about 5 and about 20 minutes.

2. A process for the production of alkenyl aromatic hydrocarbons, which comprises reacting an alkylatable aromatic hydrocarbon with a normal 1,3-diolefin at a reaction temperature not greater than about 150° F. in the presence of a catalyst comprising a liquid complex containing equimolar quantities of a monohydric aliphatic alcohol and a boron trihalide and resulting from saturating a monohydric aliphatic alcohol with a boron trihalide and maintaining a reaction time between about 5 and about 20 minutes.

3. A process for the production of alkenyl aromatic hydrocarbons, which comprises reacting an alkylatable aromatic hydrocarbon with a normal 1,3-diolefin at a reaction temperature not greater than about 150° F. in the presence of a catalyst complex consisting of substantially one mol of boron trifluoride per mol of an alcohol.

4. A process for the production of phenyl butene, which comprises reacting benzene and 1,3-butadiene, with a substantial molar excess of benzene, at a reaction temperature such that the major portion of the resulting reaction products is phenyl butene and reaction products comprising polymers of phenyl butene, polymers of butadiene, and diphenyl butane are together no more than a minor portion of said resulting reaction products, in the presence of an addition compound resulting from saturating an aliphatic monohydric alcohol with boron trifluoride, whereby essentially one mol of boron trifluoride reacts with one mol of said alcohol, and recovering a material comprising phenyl butene so produced from effluents of said reaction.

5. A process for the production 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 consisting of substantially one mol of a boron trihalide per mol of an alcohol.

6. 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 under alkenylation conditions in the presence of a catalyst complex consisting of substantially one mol of boron trifluoride per mol of a monohydric aliphatic alcohol having not more than six carbon atoms per molecule.

7. A process for the alkenylation of an aromatic hydrocarbon, which comprises reacting 1,3-pentadiene with a molar excess of an alkenylatable aromatic hydrocarbon under alkenylation conditions in the presence of a catalyst complex consisting of substantially one mol of boron trifluoride per

mol of a monohydric aliphatic alcohol having not more than six carbon atoms per molecule.

8. A process for the alkenylation of an aromatic hydrocarbon, which comprises reacting 1,3-butadiene with a molar excess of an alkenylatable aromatic hydrocarbon under alkenylation conditions in the presence of a catalyst complex consisting of substantially one mol of boron trifluoride per mol of a monohydric aliphatic alcohol having not more than six carbon atoms per molecule.

9. A process for the production 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 containing equimolar quantities of an alcohol and a boron trihalide and resulting from substantially saturating an alcohol with a boron trihalide at a temperature not greater than about 150° F.

10. A process which comprises reacting an alkenylatable aromatic hydrocarbon with an open chain 1,3-diolefin at a reaction temperature such that the major portion of the resulting reaction products is 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, in the presence of a catalyst resulting from saturating an aliphatic monohydric alcohol with boron trifluoride, whereby essentially one mol of boron trifluoride reacts with one mol of said alcohol, and recovering a material comprising said alkenyl derivative of said aromatic hydrocarbon so produced from effluents of said reaction.

WILLIAM N. AXE.

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