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CATALYTIC ALKYLBENZENE SYNTHESIS

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7 Claims. (Cl. 260—668)

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This invention relates to synthesis of alkylbenzene compounds, and particularly alkylbenzenes of carbon content suitable for conversion to detergents, wetting agents and the like, e. g. sulfonated alkylbenzene detergents. The detergent range alkylbenzene compounds prepared in accordance with this invention are characterized by alkyl groups of between 7 and 21 carbon atoms and can have additionally a second alkyl group of not more than 10 carbon atoms or another substituent such as chloro or hydroxy.

Conventional methods for production of alkylbenzenes involve alkylation of benzene with a long chain chlorinated petroleum fraction in presence of a condensation catalyst such as aluminum chloride. It has also been proposed to use long chain olefins or polymer olefins to provide detergent range alkyl chain upon condensation with benzene. In these alkylbenzenes, the phenyl groups are mostly attached to secondary carbon atoms along the alkyl chain.

A further proposal for alkylating the benzene ring, giving normally relatively high molecular weight waxy products which may contain a certain proportion of alkylbenzene hydrocarbons in the detergent range, is to heat a short chain alkyl substituted benzene with ethylene under pressures in the range of 400–1500 atmospheres (6,000–22,500 p. s. i.) and at temperatures of about 200–300° C. at which reaction begins, in presence of certain nitrogen compound catalysts including certain oximes and azines.

Advantages of my process described below over prior processes known to me for producing alkylbenzenes include easy purification of product, use of readily available catalysts, use of relatively low pressures, and obtainment of high space-time yields of the desired products.

My process for preparing alkylbenzene compounds comprises reacting in presence of a peroxy catalyst as defined below and at temperatures between about 200° C. and about 350° C., and at pressures between about 500 and about 5000 p. s. i., ethylene and an alkylbenzene compound in which the benzene ring contains in all not more than 2 substituent groups, and substituent alkyl groups contain not more than 10 carbon atoms each, and have at least one hydrogen atom attached to a carbon atom alpha to the benzene ring; additionally in accordance with my process, mol ratios of alkylbenzene compound reactant:ethylene are at least about 0.5:1, preferably above about 1:1.

In general reaction temperatures of about 260° C. and above are preferred as giving higher yields

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of products and bringing most of the product into the detergent range. At temperatures about 260°–300° C., conditions favoring detergent range product include pressures of about 2000 to about 3000 p. s. i. with amount of alkylbenzene compound reactant, expressed as volume of the liquid at room temperature (15°–35° C.) between about 35% and about 60% of the volume of the reaction space. At lower pressures and with larger amounts of alkylbenzene reactant, the space-time yields become progressively smaller; and at high pressures and small amounts of alkylbenzene compound reactant (i. e. at low alkylbenzene reactant:ethylene mol ratios), the products contain increasing proportions of straight ethylene polymers and waxy aralkyl products boiling above the detergent range. At higher reaction temperatures, above 300° C., the products remain mostly in the detergent range even using higher pressures, e. g. 4000–5000 p. s. i., in conjunction with the same amount of alkylbenzene reactant, namely a volume, measured in liquid state at room temperatures, of 35–60% of the volume of the reaction zone.

An unusual feature of my process, contributing importantly to its successful operation, is use of temperatures considerably higher, e. g. 50°–150° C. higher, than necessary for reaction to proceed under the prevailing conditions of catalyst and pressure. These elevated reaction temperatures favor production of alkylbenzenes mostly having alkyl chains in the detergent range of about 7–21 carbon atoms and also sharply increase space-time yields of alkylbenzene product. Too high reaction temperatures, however, are undesirable in that they promote formation of impurities which are not readily sulfonated. Particularly favorable results in terms of detergent range alkylbenzene production are obtained at temperatures of about 275° C.–320° C.

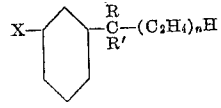
The temperatures employed in my process impose restrictions on the catalyst which can be used. It must decompose smoothly and non-explosively at these elevated temperatures yet to be of interest, it must have pronounced catalytic effect. Of a variety of peroxy, nitrogen containing, chlorine containing and other catalysts of free radical reactions which were tested, most appeared ineffective and none equaled hydroperoxides in effectiveness as measured by yields of products with at least about 90% by weight having C_7–C_{21} alkyl groups. Among the hydroperoxides, cumene hydroperoxide was outstanding. Others which can be used to good advantage are hydrogen peroxide, tetralin hydroperoxide, and

alkyl hydroperoxides such as tertiary butyl hydroperoxide and the crude hydroperoxide products obtained upon passing air through hydrocarbons, such as petroleum, in liquid phase. Other peroxy catalysts which are stable, or only slowly decompose, below about 100° C. can also be used, e. g. benzoyl peroxide, di-tertiary butyl peroxide, di-2-phenylpropyl-peroxide-2, etc.

The alkylbenzene compound reactant employed in my process has one alkyl group containing not more than 10 carbon atoms and has at least one hydrogen atom attached to a saturated carbon atom alpha to the benzene ring. The compound can have another alkyl group containing not more than 10 carbon atoms as additional substituent in the benzene ring or can have other additional substituent such as chloro or hydroxy. The 2 substituents permitted can take the form of a polymethylene ring attached at 2 points to the benzene ring as in tetralin; and the alkyl group can itself contain substituents. Specific compounds which have been found operative in my process are toluene, ethylbenzene, isopropylbenzene (i. e. cumene), normal amylbenzene, octylbenzene, xylene, para-isopropyltoluene, tetralin, diphenylmethane, orthochlorotoluene, parachlorotoluene and paracresol.

Different compounds display different activity in my process as measured by the space-time yields of product. Chain branching at the alpha carbon atom of the alkyl group appears to promote activity as long as at least one hydrogen remains attached to this carbon atom. Toluene and cumene are representative, respectively, of relatively inactive compounds and relatively active compounds in their behavior in my process. Since these compounds are readily available they are taken for purposes of illustrating my process in the examples below.

The products obtained by my process are a liquid mixture of alkylated benzene compounds, narrow in terms of carbon content of the alkyl chains. Chemically their structure can be represented by the formula:



where X, R and R′ are hydrogen or a substituent such as in the active starting materials listed above and n is an integer which under preferred conditions of operation will be between 3 and 10, inclusive, for most of the product.

The 7–21 carbon alkylbenzene products of my process can be separated from any side products by simple distillation to give a distillate which can be used directly with excellent results for sulfonation to detergent. In an embodiment of my invention which is preferred for producing particularly narrow mixtures of detergent range alkylbenzene compounds, crude product from toluene, or like starting alkylbenzene having a CH_2 group attached to the benzene ring, is distilled and low boiling products, (alkylbenzene products with about C_7–C_{10} alkyl groups and at least one hydrogen atom on a carbon attached to the benzene ring) are returned to the reaction zone wherein they react along with additional quantities of starting alkylbenzene compound and form additional product of the desired alkyl chain length, say C_{11}–C_{21}. Contrary to what might be expected, presence of recycled low boiling product fractions in the reaction mixtures leads to no increase, but instead actually appears to reduce formation of high boiling residue of carbon content above the detergent range.

While the principles of operation of my process are not entirely clear, the process apparently involves formation and interaction of free radicals including polyethylene-containing free radicals and radicals obtained by abstraction of hydrogen from carbon alpha to the benzene nucleus. The degree of polymerization reached by the polyethylene chains introduced during reaction into the alkylbenzene reactant appears to be a complex function of temperature, pressure, catalyst and quantity of alkylbenzene reactant present in the reaction zone. My preferred process conditions outlined above and described in more detail below in connection with the examples which follow result in product which is liquid and substantially all of which contains only 3–10 molecules of ethylene incorporated therein.

The following examples are specific embodiments illustrative of my invention, but are not to be understood as limiting the same.

Example 1A.—A pressure-resistant stainless steel autoclave of 1820 cc. capacity provided with rocker and thermostatic temperature control was charged at room temperature with 900 cc. of toluene under an ethylene atmosphere. Commercial ethylene was then introduced from high pressure storage and the autoclave was heated to reaction temperatures of about 260° C. and pressures of about 2000 p. s. i. A solution of cumene hydroperoxide in toluene, containing about 5 grams of cumene hydroperoxide, was injected into the autoclave at reaction temperatures to give a total toluene charge of 940 cc. and cumene hydroperoxide concentration of about 0.65 weight percent based on the toluene charge. The mol ratio of aralkyl reactant:ethylene resulting was about 2:1. Reaction conditions were maintained for 6 hours with intermittent additions of ethylene to maintain reaction pressures. The vessel was then cooled, bled of excess ethylene and discharged.

The product was separated into 3 fractions by first distilling off excess toluene, then distilling the remaining material at about 1–2 mm. pressure. The first fraction was material boiling below about 110° C., the second fraction was material boiling between about 110° C. and about 220° C. and the third fraction was residue. By careful fractionation of composite samples from a number of runs, and analysis and molecular weight determination of the fractions thus obtained, it was found that the material boiling below about 110° C./1 mm. was a mixture of alkylbenzenes mostly having 7, 9 and 11 carbon atoms in the alkyl group and the material boiling 110°–220° C./1 mm. was a mixture of alkylbenzenes mostly having between 13 and 21 carbon atoms in the alkyl group.

81 grams of alkylbenzene products were obtained by the above outlined procedure of which 54 weight percent (43.7 grams) was in fraction 1, 36 weight percent (29.2 grams) was in fraction 2 and 10 weight percent (8.1 grams) was residue.

Under like conditions to the preceding except that the weight of cumene hydroperoxide was quadrupled, the total yield of product was 116 grams of which 56 weight percent was in fraction 1, 40 weight percent was in fraction 2 and 4 weight percent was residue.

By way of comparison, under like conditions to

the preceding except that no catalyst was added the yield of products amounted to about 10 grams.

B. Using about 5 grams of cumene hydroperoxide catalyst and reaction temperatures of 300° C., with conditions otherwise as in part A, 94 grams of products were obtained of which 66 weight percent was in fraction 1 and 24 weight percent was in fraction 2 with 10% of residue. Under like conditions except that reaction temperatures were 340° C. the yield of product was 146 grams with 78 weight percent in fraction 1, 22 weight percent in fraction 2 and no residue.

C. Using about 5 grams of cumene hydroperoxide catalyst and 840 cc. of toluene instead of 940 cc. in the charge under conditions otherwise like those of part A, the mol ratio of toluene:ethylene is about 1.7 and the yield of products was 92 grams instead of 81 grams as in part A, 51.5 grams in fraction 1, 26.7 grams in fraction 2, and 13.8 grams residue amounting to about 15 weight percent of the products instead of 10 weight percent.

Under these part C conditions but with 9 cc. of 30% aqueous hydrogen peroxide substituted for cumene hydroperoxide catalyst a yield of 33 grams of alkylated toluene was obtained, all of which boiled below 220° C./0.5 mm.

D. When the charge of toluene was 740 cc., at reaction temperatures of 320° C. instead of 260° C., with conditions otherwise as in part A above, the yield of products after 6 hours amounted to 213 grams of which 40% was in fraction 1 and 60% in fraction 2 with no residue. Toluene:ethylene mol ratio under these conditions is about 1.4:1.

Example 2A.—840 cc. of cumene and about 5 grams of cumene hydroperoxide catalyst were heated with ethylene as in the preceding example at reaction temperatures of about 260° C. and pressures about 1000 p. s. i. The yield of alkylbenzene products was 109 grams of which 95% boiled below about 220° C. at 1 mm. pressure, after removal of cumene.

B. When pressures were increased to about 1500 p. s. i. under conditions otherwise as given above in this example, the yield of alkylbenzene products increased to 160 grams and the residue amounted to about 11 weight percent.

C. With total pressures about 2000 p. s. i., similar results to those at 1500 p. s. i. were obtained employing 1040 cc. of cumene as above in this example.

D. Using in the above procedure 840 cc. of cumene, 2000 p. s. i. pressure, 260 C. temperatures, and about 17 grams of cumene hydroperoxide catalyst gave a product yield of 282 grams of which 88 weight percent was in fractions 1 and 2 and 12 weight percent was residue.

Example 3.—845 cc. of toluene and 95 cc (86 grams) of alkylbenzene products of fraction 1 above-identified obtained as in Example 1A above were heated as above-described in Example 1A in presence of about 5 grams of cumene hydroperoxide catalyst. The yield of alkylbenzenes obtained by distillation as above-described was 133 grams of which 67 weight percent (89 grams) was in fraction 1 and the remainder (44 grams) was in fraction 2. As compared to the tests of Examples 1A and C, under like conditions but without recycled low boiling products in the alkylbenzene feed, the yield in fraction 2 was about 50% greater, and no residue was obtained.

Fractions of the above alkylbenzene products were sulfonated in usual manner, e. g. with equal weight of 30% oleum added at minus 10° C. and

stirred 2–3 hours at room temperatures; allowed to stand to separate a layer of excess acid; neutralized by 20% aqueous sodium hydroxide with ice bath cooling; dried on a drum drier and purified by extraction of any oil with acetone or toluene. 100% H_2SO_4 was also used as sulfonating agent. Sulfonation was quantitative or practically so. Especially with alkylbenzenes formed at relatively elevated temperatures such as 320° C., washing the crude product before sulfonation with about 10–15 weight percent of 100% sulfuric acid somewhat improved the detergency of the final sulfonated salt.

The products were tested in the washing of woolen cloth at concentrations of 0.4%, 0.2% and 0.1%. Results varied somewhat with boiling range of fraction, method of sulfonation, purification treatment, builders and other additives used, etc. Fractions boiling over the range of about 110° C. to about 150° C. at 0.3 mm. pressure were found to form upon sulfonation good detergents similar to commercial alkylbenzene sulfonate detergents, with individual results of particular tests well above those obtained with commercial detergents under identical conditions. These fractions are alkylbenzenes having in the alkyl chain about 13 to about 17 carbon atoms.

Inclusion of materials boiling down to about 30° C. and/or up to about 200° C./0.3 mm. still left my alkylation products good to excellent intermediates for sulfonation to detergent even though these lower and higher boiling fractions alone showed upon sulfonation little or no detergency. The low boiling fractions just mentioned are alkylbenzenes having about 7 to about 11 carbon atom alkyl chains and the high boiling fractions similarly have about 19 to about 21 carbon atom side chains.

Inclusion of increasing quantities of still higher boiling material rapidlly reduces detergency of the final sulfonate.

The ethylene and alkylbenzene reactants employed in my process can be commercial products not requiring special purification. Preferably, the ethylene contains not more than about 10% by volume of impurities such as propylene, nitrogen and methane and not more than about 0.1% by weight of oxygen. Larger amounts of the impurities named are tolerable and tend to decrease the quantities of residue but tend also to decrease space-time yields.

Quantities of catalyst are suitably in the range between about 0.1% and about 5% by weight on the alkylbenzene reactant. Much of the catalytic effect is usually obtained by use of about 0.5–1% of catalyst by weight on the alkylbenzene reactant, with relatively small increase in yield for larger amounts, and accordingly use of 0.5–1 weight percent of catalyst is generally preferred. Increasing amounts of catalyst tend to decrease the amount of residue formed.

Reaction times employed in the examples are about 6 hours. Such times are sufficiently long to minimize effects of heating up and cooling down the reactor. Reaction can be continued longer, with yields continuing to increase; and substantial yields can be obtained in much shorter times, e. g. 15 minutes.

As illustrated in Example 3 above, addition of recycled low boiling product fraction, e. g. from toluene in quantities of about 10 volume percent in toluene feed, leads to increased space-time yields of desired products and elimination

of by-product. Larger proportions of recycle can also be used, e. g. 20% and more.

My process has been illustrated in the examples by batch operations but can be operated continuously under like conditions of temperature, pressure, catalyst concentrations, and alkylbenzene reactant:ethylene mol ratio.

I claim:

1. Process for producing alkylbenzene compounds which comprises reacting, in the presence of peroxy catalyst, having no elements other than carbon, hydrogen and oxygen in the molecule and which is substantially stable below about 100° C., and at temperatures between about 200° C. and about 350° C., and at pressures between about 500 and about 5000 p. s. i., ethylene and alkylbenzene compound in which the benzene ring contains in all not more than 2 substituent groups and substituent alkyl groups contain not more than 10 carbon atoms each, said alkylbenzene compound having at least one hydrogen atom attached to a saturated carbon atom alpha to the benzene ring; and establishing mol ratios of alkylbenzene reactant:ethylene at least about 05:1.

2. Process as defined in claim 1 wherein pressures are between 2000 and 5000 p. s. i., alkylbenzene reactant occupies, measured as a liquid at room temperature, about 35%–60% of the volume of the reaction zone, and catalyst is a hydroperoxide.

3. Process as defined in claim 2, wherein alkylbenzene reactant comprises cumene and catalyst is cumene hydroperoxide.

4. Process as defined in claim 2, wherein alkylbenzene reactant comprises toluene and catalyst is cumene hydroperoxide.

5. Process as defined in claim 4, wherein pressures are between about 2000 and about 3000 p. s. i. and temperatures in the reaction zone are in the range between about 260° C. and about 300° C.

6. Process as defined in claim 5, wherein alkylbenzene reactant is toluene and recycled relatively low boiling alkylbenzene products of said process.

7. Process as defined in claim 1, wherein starting alkylbenzene reactant is at least one material of the group consisting of toluene, ethylbenzene, cumene, normal amylbenzene, octylbenzene, xylene, para-isopropyltoluene, tetralin, diphenylmethane, ortho-chlorotoluene, para-chlorotoluene and para-cresol and catalyst is at least one material of the group consisting of cumene hydroperoxide, tetralin hydroperoxide, and hydrogen peroxide.

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