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PROCESS FOR THE MANUFACTURE OF AROMATIC SUBSTITUTED ALKANES

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ABSTRACT OF THE DISCLOSURE

Aromatic substituted straight chain alkanes, having a low content of isomers in which the aromatic substituent occupies the 2 position on the alkyl chain are prepared by alkylation of aromatics with straight chain alpha-olefins in the presence of a hydrogen fluoride catalyst and a paraffin having from about 4 to 32 carbon atoms. Sulfonates of the products produced are particularly useful in detergent compositions.

This invention relates to methods for the manufacture of arylalkanes and alkylphenols and more specifically, the invention relates to methods for producing arylalkanes and alkylphenols having a relatively low content of isomers in which the aromatic substituent is in the 2 position on the alkyl chain.

It is known that sulfonates of arylalkanes and ethoxylated alkylphenols prepared from straight chain alkenes have different properties depending upon the position of the aromatic substituent upon the aliphatic group and while for some applications a product containing a high percentage of compounds in which the aromatic substituent is near one end of the aliphatic chain is desirable, for most applications in the surface active field arylalkane and alkylphenol products are desired containing relatively low amounts of isomers in which the aromatic substituent is in the 2 position on the alkyl chain. When the starting alkene is one in which the double bond is centrally disposed in the aliphatic chain, an alkylation product is usually obtained which has a relatively low content of isomers in which the aromatic group is positioned near one end of the alkyl chain but when the starting alkene is a straight chain alpha-olefin, the alkylation product normally has a content of isomers in which the aromatic substituent is in the 2 position of the alkyl chain which is so high as to make the product less than most desirable for some uses. Numerous processes have been reported for obtaining from alpha-olefins arylalkane products containing low amounts of 2-arylalkane isomers, but many of these processes require a separate processing operation and, in some instances, even with the use of an added process step, the 2-arylalkane isomer content of the product is still in excess of about 20% to 30%. It will be seen, therefore, that a process for the production, from straight chain alpha-olefins, without an extra processing step, of a product having an exceedingly low content of isomers in which the aromatic substituent is then in the 2 position would be an advance in the art.

It has now been found in accordance with this invention that in the reaction of a straight chain alpha-olefin with a monocyclic aromatic hydrocarbon or a monocyclic phenol using an HF catalyst, the presence of a paraffin material greatly reduces the quantity in the alkylation product of isomers in which the aromatic substituent is in the 2 position. In fact, the reduction in most instances is at least as great as that which could be obtained by subjecting the starting alkene to a separate isomerization process and the 2-isomer content of the product closely approaches that which could be obtained

under similar conditions using a pure alkene material containing only the isomer in which the double bond is in a central position. The paraffin diluent can suitably be added to the reactor simultaneously with the reactants and can be recovered in the distillation operation conventionally performed subsequent to the alkylation so that the process does not require any additional process step and does not result in the consumption of a substantial quantity of any additional raw material.

Any paraffin material can suitably be employed in the process of this invention and one can use straight chain paraffins, branched chain paraffins, or cyclo-paraffins alone or in admixture with each other. Straight chain paraffins and unsubstituted cyclo-paraffins are preferred because the presence of a secondary or tertiary carbon atom in the paraffin increases its reactivity in the presence of HF and can under adverse conditions result in undesired side reactions. The choice between straight chain paraffins and unsubstituted cyclo-paraffins is dictated largely by availability, but in some instances, the boiling point or solubility of the paraffin in the reactants will have a bearing upon one's choice. It is desirable that a paraffin material be selected which has a boiling point different from that of the aromatic reactant used in the manufacture of the arylalkane product and different from that of any of the isomers normally present in the reaction product so that the paraffin material can readily be recovered for reuse by distillation. Also, it is desirable to select a paraffin material that is readily soluble at the selected level of use in the raw material mixture and also in the individual reactants so that the formation of a separate paraffin phase is avoided. The latter consideration presents no real problem since almost all paraffin materials are miscible with the usual alkenes and aromatic hydrocarbons utilized in the production of arylalkane and alkylphenol detergent intermediates.

The chain length or number of carbon atoms in the paraffin material is of little or no importance as long as the paraffin material has the desired physical characteristics because, as set forth above, the paraffin is normally inert in the reaction mixture and is recovered unchanged upon the completion of the reaction. Generally, a paraffin should be selected which has a boiling point at least as high as the maximum reaction temperature to be employed but not so high that it cannot be recovered from the high boiling still bottoms by distillation. Similarly, as set forth above, a chain length can be selected to provide a boiling point different from that of the unreacted raw material and any of the desired isomers of the product to facilitate recovery of the paraffin material. If the reaction is to be conducted at a very low temperature and/or under pressure, it is possible to employ a material having as few as 4 carbon atoms such as n-butane or cyclobutane. At the other extreme, it is possible to employ paraffins having as many as about 32 carbon atoms as illustrated by petroleum waxes although in some instances solubility and recovery problems are encountered when employing such materials. Normally, it is preferred to use a paraffin material having from 5 to 15 carbon atoms and illustrative examples of preferred materials include n-hexane, cyclo-hexane, n-heptane, and n-dodecane.

Within limits, the amount of paraffin employed has a bearing upon the quantity of 2-arylalkanes or 2-hydroxyarylalkanes in the alkylation product and if one desires only a slight reduction in the content of such isomers in the product, it is only necessary in accordance with this invention to employ as little as about 5% by weight, based upon the weight of alkene reactant, of paraffin. In most instances, however, one will desire a relatively large reduction in the 2-arylalkane or 2-hydroxyarylalkane isomer content of the reaction product and will employ an amount of paraffin equal to at least about 50% by weight, based upon the weight of alkene reactant. It is seldom, if ever, advantageous to employ the paraffin material in an amount such that the weight ratio of paraffin to alkene is more than about 10:1 since the use of more than this amount of paraffin does not give a corresponding reduction in the 2-arylalkane or 2-hydroxyarylalkane isomer content of the product, necessitates the handling of larger quantities of materials and, in addition, increases the cost of product and paraffin recovery. However, except for these disadvantages, the addition of large excesses of paraffin is not objectionable and satisfactory results can be obtained using, for example, a weight ratio of paraffin material to alkene of 50 to 1. In most instances, the preferred amount of paraffin material to be employed is from about 100% to 1000% by weight, based upon the weight of alkene reactant or, in other words, a weight ratio of paraffin to alkene of from about 1:1 to about 10:1.

In accordance with a preferred embodiment of the invention, the paraffin material is divided into two quantities and a first portion thereof is mixed with at least a portion of the aromatic reactant, for example from 10% to 100% thereof, and the desired quantity of HF catalyst. The second portion of the paraffin material is then mixed with the alkene reactant and the remainder, if any, of the aromatic reactant. The two mixtures are then mixed together over a period of time preferably with constant agitation to eliminate the possibility of localized concentration of reagents and undesired temperature gradients within the reaction mixture. Normally, it is desirable that the portions of the paraffin material be approximately equal, and if the paraffin is divided into unequal proportions, the larger proportion should be added to the catalyst containing mixture before the alkene is mixed therewith. Preferably, from about 40% to 90% by weight of the paraffin should be added to the catalyst containing mixture but satisfactory results can be obtained by adding 100% of the paraffin to the catalyst mixture or any other percentage as long as the catalyst mixture contains an amount of paraffin equal to about 5% by weight of the alkene reactant at the time mixing of the alkene reactant with the catalyst is initiated.

Except as set forth above, the process of this invention can be conventional and can be employed in the production of substantially any arylalkane or alkylphenol product which has been conventionally employed in the manufacture of detergent surface active agents. The aromatic hydrocarbon most frequently employed in the manufacture of detergent intermediates is benzene, and the phenolic compound most frequently employed is phenol. However, other monocyclic aromatic hydrocarbons and phenols can suitably be employed in the process, and suitable examples include resorcinol, ortho-cresol, toluene, xylene, and cumene. Any aliphatic hydrocarbon substituent group or groups on the aromatic nucleus should in each instance be saturated to prevent side reactions and the total number of substituents, including hydroxy groups, on the aromatic nucleus preferably should not be more than 2 or 3 in number. In most instances, the aromatic reactant will contain not more than about 9 carbon atoms, although this limitation is dictated by availability and desirability for use in the manufacture of detergent intermediates, and if desired, the invention can be used with aromatic reactants containing 12 or 15 or more carbon atoms.

Straight chain alpha-olefins which can suitably be employed in the process of this invention include any of those conventionally employed in the manufacture of detergent intermediates. In most instances, the alpha-olefins will have from 8 to 24 carbon atoms, and alpha-olefins having a molecular chain length of from 10 to 20 carbon atoms are preferred. Commercial alpha-olefins are usually mixtures rather than substantially pure materials and such mixtures having average molecular chain lengths within

the above ranges are quite suitable for use in the process of this invention.

As in conventional practice, it is usually advantageous in accordance with this invention to employ an aromatic to olefin molar ratio of at least about 1:1 because the use of a lower ratio results in excessive formation of high boiling by-products. There is no upper limit as to the aromatic to olefin molar ratio except that dictated by convenience and the economics of recovering unreacted raw materials, and an aromatic to olefin ratio as high as 100:1 can suitably be employed, but the preferred aromatic to olefin ratio is generally from 1½:1 to 10:1. Varying the aromatic to olefin ratio in most instances has no marked effect upon the 2-arylalkane or 2-hydroxy arylalkane content of the product but does affect in a conventional manner the nature and amount of by-products produced.

The amount of catalyst to be employed can be conventional and can range from about 10% by weight, based upon the weight of alkene material in the reaction mixture, to an upper limit dictated only by convenience and one can, for example, with satisfactory results, employ an amount of catalyst sufficient to provide a weight ratio of catalyst to total olefin of as high as 20:1. If desired, one can even employ in accordance with the procedure described and claimed in United States application, Ser. No. 553,030, filed concurrently herewith, such a small amount of catalyst, for example, as little as 0.2% by weight based upon the over-all weight of the reaction mixture, that a separate catalyst phase is not obtained, but this results in a marked increase in the 2-arylalkane isomer content of the product as compared to the minimum which can be obtained employing the process of the present invention and in most instances is not desirable. In most instances, a preferred amount of catalyst is that which will provide a weight ratio of catalyst to total olefin reactant of from 1:2 to 10:1.

The temperature at which the reaction is conducted in accordance with this invention can be conventional, and for example, can range from the freezing point of the reaction mixture to about 200° C. or even higher, but the preferred operating temperature range is from about −10° C. to 80° C. with temperatures of from about −5° C. to 60° C. being especially preferred. A change in operating temperature in most instances results in a significant change in the proportion of 2-arylalkane or 2-hydroxyarylalkane isomers in the product with low reaction temperatures favoring decreased amounts of the 2-arylalkane or 2-hydroxyarylalkane isomers in the product. For example, it has been found that a reduction in temperature of from 55° C. to 0° C. can in some instances result in a much as 7% to 8%, based on the over-all weight of the product, reduction in the percent of 2-phenyl isomers in the product.

The pressure under which the alkylation reaction is conducted can be varied within a wide range as long as the pressure employed is not so low as to result in the vaporization of raw materials or excessive catalyst loss. Suitable operating pressures can vary from about 0.5 to 10 atmospheres with the preferred pressure range being from about 1 to 4 atmospheres.

The invention will now be illustrated by the following specific examples in which all parts are by weight unless otherwise indicated:

EXAMPLE I

(A) A mixture of 200 parts of benzene and 200 parts by weight of anhydrous HF is placed in a suitable alkylation apparatus and heated at 55° C. under 40 pounds p.s.i.g. pressure. At a temperature of 55° C., it has been found that the pressure should be maintained at least about 40 p.s.i.g. to avoid catalyst loss. A mixture of 100 parts of alpha-dodecene and 100 parts of benzene is then added with constant agitation over a period of ten minutes, and the reaction mixture is retained for an additional ten minutes at 55° C. with constant agitation. The mixture is then cooled to 6° C. and allowed to stand for one hour after which time the organic layer is separated from the catalyst layer by decantation. The separated organic layer is then distilled to remove unreacted benzene and dissolved HF catalyst and a sample of the thus purified product is analyzed by vapor phase chromotography to determine the isomer distribution.

(B) The procedure of A above is repeated except that 800 parts by weight of n-hexane are added to the mixture of HF and benzene, and 200 parts by weight of n-hexane are added to the mixture of alpha-dodecene and benzene.

(C) The procedure of B above is repeated except that in place of a weight ratio of paraffin to olefin of 10:1, a weight ratio of paraffin to olefin of 50:1 is utilized.

In actual tests of the above procedures, the following results were obtained:

	Procedure A (no n-hexane)	Procedure B (n-hexane: P/O=10)	Procedure C (n-hexane: P/O=50)
2-phenyldodecane	25.2	13.7	13.9
3-phenyldodecane	16.9	15.1	16.1
4-phenyldodecane	17.4	16.2	18.1
5- + 6-phenyldodecane	40.6	55.0	52.0

For comparative purposes, the procedures of this example were used to alkylate benzene with dodecene-6 and even starting with an olefin in which the double bond is centrally disposed, it was only possible to reduce the 2-phenyldodecane content of the product to 13.6% (14.8% when no n-hexane was employed), thus illustrating that the process of this invention makes possible using pure alpha-olefins or mixtures of alpha-olefins and internal olfeins, results which were heretofore obtainable in a single step process only by using a pure olefin material in which the double bond is centrally disposed with respect to the aliphatic chain.

EXAMPLE II

The procedures of Examples I–B and I–C are repeated except that in place of a reaction temperature of 55° C., a reaction temperature of from 0° C. to 5° C. is employed.

In actual tests of the above procedures, the following results were obtained:

	Dod-1(P/O=10:1)	Dod-1(P/O=50:1)
2-phenyl	12.0	11.4
3-phenyl	13.7	14.0
4-phenyl	19.8	18.6
5- and 6-phenyl	54.5	56.0

By comparing the results obtained in Example I with those obtained in Example II, it will be seen that improved results are obtained using low reaction temperatures.

EXAMPLE III

(A) A mixture of 200 parts by weight of benzene and about 200 parts of anhydrous HF is placed in a suitable alkylation apparatus and heated to 55° C. maintaining a pressure of 40 p.s.i.g. to insure the presence of a liquid HF phase. There is then added to the catalyst mixture over a period of about ten minutes and with constant agitation a mixture containing 25 parts by weight of alpha-dodecene, 25 parts by weight of alpha-tetradecene, 25 parts by weight of alpha-hexadecene, 25 parts by weight of alpha-octadecene, and 100 parts by weight of benzene. Stirring is then continued for at least about ten additional minutes, and the mixture is cooled to 6° C. and allowed to stand for one hour. The organic layer is then separated and distilled to remove unreacted benzene and dissolved HF catalyst and a sample of the thus purified product is analyzed by vapor phase chromotography to determine the isomer distributions of the various alkylbenzenes.

(B) An alkylation reaction is conducted substantially as described in A above except that to the catalyst mixture there is added prior to the initiation of the reaction 800 parts by weight of n-hexane, and to the olefin benzene mixture there is added prior to the initiation of the reaction 200 parts by weight of n-hexane.

In actual tests of the above procedures, the isomer distributions of the phenyldodecanes in the products were substantially the same as set forth in Example I, and the isomer distributions of the other phenylalkanes were as follows:

	Procedure A (non-hexane)			Procedure B (n-hexane added)		
Percent Isomer	C_{14}	C_{16}	C_{18}	C_{14}	C_{16}	C_{18}
2-phenyl	24.4	32.4	31.4	11.9	11.6	11.8
3-phenyl	15.3	12.5	14.7	13.7	11.3	9.1
4-phenyl	13.3	7.3	8.4	13.5	11.7	8.3
5-phenyl	13.5					
Rest	33.5	47.8	45.5	59.9	65.4	70.8

The procedure when employing other paraffins, aromatic reactants and alpha-olefins can be the same as illustrated in the above examples.

What is claimed is:

1. In a process for the manufacture of aromatic substituted alkanes wherein an aromatic compound is reacted with an alkylation agent consisting essentially of a straight-chain alpha-olefin of from about 8 to 24 carbon atoms in the presence of hydrogen fluoride catalyst, said aromatic compound being selected from the group consisting of monocyclic aromatics having not more than 15 carbon atoms and in which the aromatic nucleus has not more than three substituents, the substituents in each instance being selected from the group consisting of hydroxy and alkyl groups, the improvement which comprises increasing the proportion of the product wherein the aromatic substituent occupies a position other than the 2 position on the alkyl chain by performing said reaction in the presence of a paraffin having from about 4 to 32 carbon atoms, the amount of said paraffin present in the reaction mixture being at least 5% by weight, based on the weight of alpha-olefin reactant, but not in excess of the solubility of the paraffin in the organic phase of the reaction mixture and not in excess of a weight ratio of paraffin to olefin of about 50:1, said reaction being performed at a temperature of from the freezing point of the reaction mixture to 200° C.

2. A process in accordance with claim **1** wherein said alpha-olefin has a molecular chain length of from 10 to 20 carbon atoms.

3. A process in accordance with claim **1** wherein the reaction temperature is within the range of about −10° C. to 80° C.

4. A process in accordance with claim **3** wherein the amount of hydrogen fluoride catalyst in said reaction mixture is maintained at a level sufficient to provide a separate liquid catalyst phase throughout the reaction period.

5. A process in accordance with claim **4** wherein said paraffin is a straight chain paraffin having from 5 to 15 carbon atoms.

6. A process in accordance with claim **5** wherein said aromatic compound is benzene.

7. A process in accordance with claim **5** wherein said aromatic compound is phenol.

8. A process in accordance with claim **6** wherein said paraffin is n-hexane.

9. A process in accordance with claim **1** wherein a first mixture is formed of at least a portion of said aromatic compound, said H.F. catalyst, and a portion of said paraffin, a second mixture is formed of said alkene reactant, the remainder, if any, of said aromatic compound and a portion of said paraffin, and said mixtures are then mixed together while maintaining the temperature of the resultant mixture within the range of −10° C. to 80° C. and while maintaining the resultant mixture under a pressure of from 0.5 to 10 atmospheres correlated with respect to temperatures to prevent catalyst loss.

10. A process in accordance with claim **9** in which the temperature of the reaction mixture is maintained in the range of —5° C. and 60° C.

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