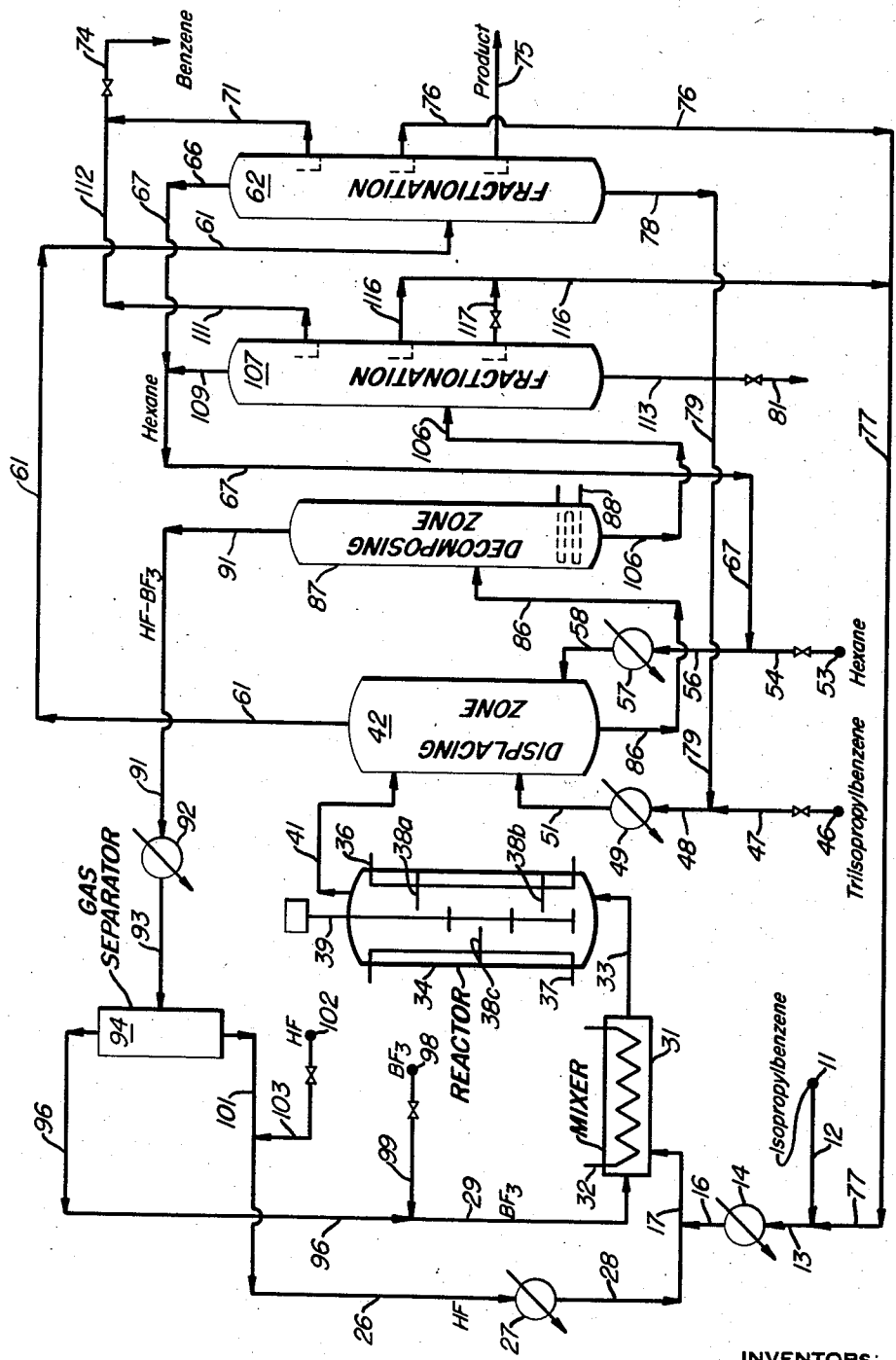


Sept. 16, 1958

A. P. LIEN ET AL
PRODUCTION OF 1-3 DI-SECONDARY ALKYL BENZENES
BY DISPROPORTIONATION
Filed Oct. 30, 1953

2,852,575



INVENTORS:
Arthur P. Lien
David A. McCaulay
BY *Michael Dufresne*
ATTORNEY

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PRODUCTION OF 1-3 DI-SECONDARY ALKYL-BENZENES BY DISPROPORTIONATION

Arthur P. Lien, Highland, Ind., and David A. McCaulay, Chicago, Ill., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application October 30, 1953, Serial No. 389,328

12 Claims. (Cl. 260—671)

This invention relates to the rearrangement of certain secondary alkylbenzenes. More particularly the invention relates to the disproportionation of isopropylbenzene and secondary butylbenzenes. Still more particularly the invention relates to the production of essentially pure meta di-isopropylbenzene and 1,3,5-tri-isopropylbenzene.

The development of the hydroperoxide synthesis for phenol has resulted in a demand for secondary alkylbenzenes. Since certain phenols have particularly desirable properties for use as chemical intermediates, a demand has arisen for large quantities of various secondary alkylbenzenes of high purity, i. e., about 95%, and also essentially pure, i. e., 99% compounds. Of particular interest are meta di-isopropylbenzene and 1,3,5-tri-isopropylbenzene. The production of di-isopropylbenzene by the alkylation of benzene with propylene produces a mixture of the three isomers; therefore, industry is concerned with the preparation of high purity individual isomers in high yield.

It is an object of this invention to prepare di-secondary alkylbenzenes by the treatment of isopropylbenzene or secondary butylbenzene. Other objects will become apparent in the course of the detailed description of the invention.

DISPROPORTIONATION

In this process a secondary alkylbenzene selected from the class consisting of isopropylbenzene and secondary butylbenzene is contacted under substantially anhydrous conditions and in the substantial absence of reactive hydrocarbons with at least an effective amount of BF_3 , preferably about 1 mol per mol of sec-alkylbenzene, and an amount of liquid HF at least sufficient to form a distinct acid phase, preferably between about 5 to 20 mols per mol of sec-alkylbenzene; the contacting is carried out at a temperature between about -30°C . and about $+80^\circ \text{C}$. for a time at least sufficient to permit an appreciable amount of rearrangement reaction; the HF and BF_3 are removed from the acid phase in order to recover poly-secondary alkylbenzene.

By operating for a sufficiently short time at a temperature between about -30°C . and about -5°C ., production of tri-secondary alkylbenzene can be essentially eliminated. Operation at temperatures below about -30°C . substantially halts the disproportionation reaction.

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The charge to the disproportionation process contains secondary alkylbenzenes selected from the class consisting of isopropylbenzene and secondary butylbenzene. In order to obtain products containing only one particular alkyl substituent, the feed must contain essentially only either isopropylbenzene or secondary butylbenzene as the reactive component.

In addition to the secondary alkylbenzene, the feed may contain non-reactive liquid hydrocarbons. It is to be understood that the term "non-reactive liquid hydrocarbons" is intended to mean those hydrocarbons which are liquid at operating conditions and which are inert to the action of the $\text{HF}-\text{BF}_3$ agent and do not participate in any reaction with the secondary alkylbenzene charged.

Examples of reactive hydrocarbons are olefins, xylene, diethylbenzene, ethyltoluene, ethyltoluene and isopropyltoluene. Examples of non-reactive hydrocarbons are: isopentane, butane and hexane. It is preferred that benzene be absent from the feed as its presence has an adverse effect on the degree of disproportionation obtained.

The process utilizes substantially anhydrous liquid hydrogen fluoride. The liquid hydrogen fluoride should not contain more than about 2 or 3% of water. Commercial grade anhydrous hydrogen fluoride acid is suitable for this process.

Under the conditions of the process, poly-alkylbenzenes form a complex containing 1 mol of BF_3 and, it is believed, 1 mol of HF per mol of polyalkylbenzene. Therefore, at least enough liquid HF must be present to participate in the formation of the complex with the poly-secondary alkylbenzene; in addition to this amount, sufficient liquid HF must be present to dissolve the complex which has been formed. In general, the presence of a distinct separate acid phase in the contacting zone indicates that at least the minimum requirement of liquid HF has been met. More than this minimum amount of liquid HF is desirable. Usually between about 3 and 50 mols of liquid HF are utilized per mol of secondary alkylbenzene charged to the process. It is preferred to operate with between about 5 and 20 mols of liquid HF per mol of secondary alkylbenzene charged.

The process requires the presence of at least an amount of boron trifluoride sufficient to cause a rearrangement reaction to take place, specifically the disproportionation of the secondary alkylbenzene to poly-secondary alkylbenzene. While amounts of BF_3 as small as 0.1 mol per mol of secondary alkylbenzene charged will cause an appreciable amount of rearrangement reaction to take place, it is desirable to operate with about 0.3 mol of BF_3 . Still more BF_3 has a beneficial effect on the degree of the rearrangement reaction and as much as 5 or more mols may be used. When high purity meta di-secondary alkylbenzene is a desired product, at least 0.5 mol of BF_3 should be used per mol of secondary alkylbenzene charged, and it is preferred to use between about 1 and about 2 mols of BF_3 per mol of secondary alkylbenzene charged, for example 0.9 mol.

When the feed to the process contains poly-alkylbenzenes in addition to the secondary alkylbenzene, 1 mol of

BF_3 should be used per mol. of said poly-alkylbenzene, in addition to that set out above.

The process may be operated with two liquid phases present in the contacting zone. At high BF_3 usages, a gas phase may also be present in the contacting zone. The two liquid phases will be spoken of herein as the raffinate phase and the acid phase. The acid phase consists of liquid HF , BF_3 , complex and physically dissolved hydrocarbons. The raffinate phase may be secondary alkylbenzenes in excess of that amount taken into the acid phase, or may be a mixture of secondary alkylbenzene and inert hydrocarbons, or may be principally inert hydrocarbons. In the absence of substantial amounts of inert hydrocarbons, the amount of raffinate phase is dependent upon the amount of BF_3 utilized. When using at least about 0.5 mol of BF_3 per mol of secondary alkylbenzene, and in the substantial absence of inert hydrocarbons, all or virtually all the secondary alkylbenzene will be taken into the acid phase either in the form of a complex or in solution. The presence of HF — BF_3 —poly-alkylbenzene complex in liquid HF very greatly increases the solubility of the liquid HF for aromatic hydrocarbons and increases slightly the solubility of paraffinic hydrocarbons.

The presence of a raffinate phase consisting principally of inert hydrocarbons, such as benzene and paraffins, has an adverse effect on the degree and direction of conversion of the secondary alkylbenzene charged, even though theoretically sufficient BF_3 is present to complex all of the poly-secondary alkylbenzene formable from the secondary alkylbenzene charged. A substantial amount of the secondary alkylbenzene will remain in the raffinate phase, even when using somewhat more than 0.5 mol of BF_3 per mol of secondary alkylbenzene charged. The secondary alkylbenzene in the raffinate phase does not undergo a rearrangement reaction to any significant extent, even under conditions of good agitation. The presence of dissolved inert hydrocarbons in the acid phase does not appear to have any adverse effect on the degree or direction of the rearrangement reactions.

In order to maximize the yield of conversion products, and to produce a di-secondary alkylbenzene product fraction consisting essentially of 1,3-di-secondary alkylbenzene, i. e., the meta isomer, it is preferred to operate under conditions which form a single essentially homogeneous liquid phase in the contacting zone. A single essentially homogeneous liquid phase is attainable with a feed containing as much as three volume percent of paraffinic hydrocarbons. Large amounts of benzene may be dissolved in the acid phase, as much as 1 mol or more, per mol of complexed poly-alkylbenzene, depending on the amount of complex in the acid phase. (It is to be understood that a separate gaseous BF_3 phase may also be present, but it is preferred that a minimum of free space be present in the contacting zone and that sufficient pressure be maintained to insure that essentially all the BF_3 is either in the complexed form or is in physical solution in the acid phase.)

The degree and direction of the disproportionation reaction are also determined by the temperature of contacting and the time of contacting; a definite relationship exists between the temperature, time and desired disproportionation products. At temperatures below about -40°C . no appreciable disproportionation takes place even at contacting times of several hours. At temperatures of about $+100^\circ\text{C}$., side reactions such as cracking occur and the direction of the disproportionation changes; gas and a wide boiling range product mixture are obtained. The practical upper limit for the operation of the disproportionation process is about $+80^\circ\text{C}$.. Appreciable amounts of disproportionation product are obtained in a not excessively long time at a temperature of about -30°C .. The preferred range of operating temperatures for the disproportionation process is between about -20°C . and about $+60^\circ\text{C}$.; wherein the

time of contacting is between about 5 minutes and 24 hours, the longer times corresponding to the lower temperatures.

The contacting time has an important effect on the course of the rearrangement reactions. At least sufficient time must be provided at the particular temperature of operation in order to obtain an appreciable amount of disproportionation products. As the contacting time is increased, at a constant temperature, the amount of disproportionation product increases. The disproportionation reaction appears to produce the di-secondary alkylbenzene as the first product. Dependent upon the temperature, a finite period of time elapses between the appearance of detectable amounts of the di-secondary alkylbenzene product and the appearance of the tri-secondary alkylbenzene product. The lower the temperature of operation, the longer the time lapse between the appearance of the di-derivative and the appearance of the tri-derivative.

With increasing contacting time, at constant temperature, the amount of tri-secondary alkylbenzene product gradually increases at the expense of di-secondary alkylbenzene formed. Gradually the amount of the tri-derivative increases and eventually the tri-derivative continues to increase with simultaneous disappearance of the di-derivative. At higher temperatures and prolonged contacting times, the reaction product mixture contains the tri-derivative as the predominant disproportionation reaction product. However, even at $+80^\circ\text{C}$. and prolonged contacting times, some secondary alkylbenzene and some di-secondary alkylbenzene will be found in the reaction product mixture. Thus by adjusting the temperature and time of contacting, it is possible to control the relative amounts of di- and tri-derivatives produced in the disproportionation process.

The disproportionation reaction can be controlled, within experimental error, to produce di-secondary alkylbenzene as essentially the only poly-secondary alkylbenzene product. When the di-secondary alkylbenzene is the only desired poly-secondary alkylbenzene disproportionation product, the contacting temperature should not exceed about -5°C .. The lower temperature of operation is about -30°C ..

The contacting time at -5°C . must be short enough to essentially eliminate the disproportionation to the tri-derivative. At about -5°C . the permissible maximum time of contacting is about 15 minutes to essentially avoid the formation of the tri-derivative. The lower the temperature of contacting, the longer the contacting time permissible for avoiding the formation of detectable amounts of the tri-derivative. At about -20°C .. contacting temperature, the permissible maximum time is on the order of 6 hours; at about -30°C ., the permissible maximum contacting time is on the order of a day or more. Thus in order to avoid the formation of appreciable amounts of tri-secondary alkylbenzene, the disproportionation process must be carried out at a temperature of about -5°C ., for a maximum contacting time of about 15 minutes. The lower the temperature of contacting, the longer will be the corresponding permissible maximum contacting time.

Even when using smaller amounts of BF_3 , the predominant di-secondary alkylbenzene product is the 1,3-di-secondary alkylbenzene, i. e., the meta isomer. The use of 0.5 mol of BF_3 and preferably about 1 mol, gives essentially pure 1,3-di-secondary alkylbenzene as the di-secondary alkylbenzene product. By careful control of the contacting time it is possible to produce a di-secondary alkylbenzene product fraction which is, within the error of the analytical procedure, pure 1,3-di-secondary alkylbenzene.

Under the conditions of operation described above, the tri-derivative is essentially pure 1,3,5-tri-secondary alkylbenzene, i. e., the symmetrical configuration.

When the charge to the disproportionation process de-

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scribed above is a secondary alkylbenzene selected from the class consisting of isopropylbenzene and secondary butylbenzene, the reaction product mixture contains relatively large amounts of the di-secondary alkyl derivative even though high temperatures and long contacting times are used. When it is desired to maximize the yield of the tri-secondary alkylbenzene product fraction, the charge to the disproportionation process should be the corresponding di-secondary alkylbenzene. The use of an isomer or a mixture of isomers of di-secondary alkylbenzene which are selected from the class consisting of di-isopropylbenzene and di-secondary butylbenzene as the charge to a disproportionation process, wherein sufficient liquid HF and BF₃ are used to form a single essentially homogeneous phase, at a temperature between about -20° and +60° C. for a suitable contacting time, results in a reaction product mixture wherein the di-secondary alkylbenzene forms only a minor part of the reaction product mixture. In the process wherein the di-derivative is the charge, it is preferred to use at least 1 mol of BF₃ per mol of charge.

When the charge to the di-secondary alkylbenzene disproportionation process consists of mixtures of the meta isomer and at least one other isomer, which other isomer is present in substantial amounts, the acid phase contains a reaction product mixture wherein the di-secondary alkylbenzene fraction is enriched with respect to the meta isomer when compared with the charge. When operating under essentially single liquid phase conditions and with at least 1 mol of BF₃ per mol of di-secondary alkylbenzene charged, the reaction product mixture contains essentially pure meta di-secondary alkylbenzene as the secondary alkylbenzene component, i. e., the ortho and/or para isomers are isomerized to the meta isomer.

The disproportionation at higher temperatures of di-secondary alkylbenzenes produces appreciable amounts of the tetra-derivative as well as the tri-derivative. Operation at lower temperatures and for short times permits holding the yield of tetra-derivative to the minimum.

However, when the tetra-derivative is the desired product, it is preferred to operate with the corresponding tri-secondary alkylbenzene as the charge to the process. Using at least 1 mol of BF₃ and sufficient liquid HF to form an essentially single homogeneous phase, tri-isopropylbenzene or tri-secondary butylbenzene are disproportionated at temperatures between about +30° C. and about +60° C. and suitable contacting times into a product mixture containing the corresponding tetra-secondary alkylbenzene as the predominant component.

The invention is limited to the HF-BF₃ treatment of isopropylbenzene isomers and secondary butylbenzene isomers because successful treatment of the secondary pentylbenzenes requires very different operating conditions. Even at temperatures on the order of +20° C. and contacting times as short as 15 minutes, the secondary pentylbenzenes undergo rearrangement of the pentyl group and also cracking of the pentyl group. In addition, cyclization reactions occur and substantial quantities of indanes and tetralins are formed. Rearrangement of the pentyl group is particularly prominent when 3-phenylpentane is the charge to the HF-BF₃ contacting zone. The 3-phenylpentane isomerizes to give good yields of the 2-phenylpentane derivative, particularly the 2,4 bis(2-pentyl) benzene disproportionation product. Rearrangement of the pentyl group is not present to any large extent when 2-phenylpentane is the charge to the HF-BF₃ contacting zone. It is to be understood that by suitable adjustment of the temperature and time of contacting it is possible to minimize side reactions.

PRODUCT RECOVERY

The reaction product mixture may be recovered from the acid phase by various methods. Probably the simplest procedure and one most suitable for laboratory work

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consists of adding the acid phase to crushed ice; or the acid phase may be contacted with cold aqueous alkaline solution, such as sodium hydroxide, potassium hydroxide and ammonia. It is desirable to prevent rearrangement reactions by the use of a cold aqueous reagent.

The hydrocarbons originally present in the acid phase appear as an upper oil layer above a lower aqueous layer. The upper oil layer may be separated by decantation and may be treated with dilute aqueous alkaline solution to remove any remaining HF and BF₃ occluded therein.

Both HF and BF₃ are relatively expensive chemicals and it is desirable in an economic process to recover these and to recycle them for reuse in the process. The HF and the BF₃ may be readily removed from the acid phase by heating the acid phase or by applying a vacuum thereto. The HF and the BF₃ distill overhead and may be recovered for reuse in the process. When di-alkylbenzenes and/or tri-alkylbenzenes are the principal complex-forming hydrocarbons, the complex may be decomposed at relatively low temperatures by the use of vacuum distillation. The tetra alkylbenzene and higher alkylbenzene complexes are stable and must be heated to relatively high temperatures, for example, 150° C. or more in order to decompose the complex.

The rearrangement reaction proceeds from the time that the complex is formed until the complex is decomposed, assuming that a suitable temperature exists. When it is desired to produce essentially only one rearrangement reaction product, for example, meta di-isopropylbenzene from para di-isopropylbenzene, or meta di-isopropylbenzene from isopropylbenzene, it is necessary to take into account the total time elapsing from the time that the complex has been formed till the time that it has been decomposed in the distillative decomposition procedure. Thus, when using distillative decomposition procedure, it is necessary to consider the residence time of the complex in the decomposing zone as a part of the contacting time. Also, it is necessary to consider the temperature maintained in the decomposing zone when a particular product or a particular ratio of products is desired. Generally the temperature in the decomposing zone should be no higher than that in the contacting zone, when operating to produce meta di-secondary alkylbenzene. The distillative decomposing zone may be operated at temperatures as low as about -20° C. by the use of high vacuum therein.

The tri-secondary alkylbenzene at moderate temperatures disproportionates very slowly to the tetra-secondary alkylbenzene. Therefore it is possible to distillatively decompose the complex of tri-secondary alkylbenzene at temperatures as high as 40 or 50° C. if the acid phase is very rapidly raised to that temperature from the reaction temperature and the HF and BF₃ are very quickly removed from the heated acid phase.

Thus the recovery of the meta di-secondary alkylbenzene product without back isomerization to ortho and para isomers or disproportionation to the tri-secondary alkylbenzene is the most difficult recovery to be made by distillative decomposition of the complex. It is obvious that operation at very low temperatures such as -10° C. or lower involves an expensive high vacuum operation since liquid HF boils at +20° C. at atmospheric pressure.

The preferred method of recovering high purity meta di-secondary alkylbenzene from an acid phase without back isomerization or disproportionation is the displacement of the meta di-secondary alkylbenzene from its HF and BF₃ complex by an alkylbenzene which forms a more stable HF and BF₃ complex. Broadly, the displacer is a polyalkylbenzene containing at least three alkyl groups which alkyl groups are selected from the class consisting of normal and secondary and which contain not more than 4 carbon atoms. Normal alkyl groups are methyl, ethyl, n-propyl and n-butyl. The secondary alkyl groups are isopropyl and secondary butyl.

Pentamethylbenzene and hexamethylbenzene are particularly effective displacers. However, the complexes formed by these compounds are so stable that quite elevated temperatures are necessary to decompose the complexes in order to recover the HF and BF_3 . Therefore, where economy is desirable, these compounds should not be used as displacers.

The preferred tri-alkylbenzenes have the symmetrical configuration, i. e., 1,3,5-tri-alkylbenzene. The preferred tetra-alkylbenzenes possess the 1,2,3,5 configuration. These displacers are preferred because they do not tend to undergo rearrangement reactions and have better displacement effectiveness than the other isomers. The preferred displacers are mesitylene, triisopropylbenzene, diisopropyltoluene and isodurene.

As it is normally impractical to operate under conditions wherein absolutely no tri-secondary alkylbenzene is produced, it is desirable to operate with a displacer which will not complicate the problem of recovering the by-product, tri-secondary alkylbenzene. Therefore it is preferred to use as the displacer in the process of this invention a poly-secondary alkylbenzene, for example, triisopropylbenzene, or tri-secondary butylbenzene, corresponding to the alkyl group charged.

Theoretically, 1 mol of added displacer will replace 1 mol of di-secondary alkylbenzene. However, greater amounts of displacer should be used. The amount of displacer used is dependent upon the total recovery of di-secondary alkylbenzene desired and also the effectiveness of the contacting of the acid phase and the displacer. It is preferred to operate with between about 2 and 4 mols of displacer per mol of di-secondary alkylbenzene present in the acid phase.

It has been pointed out that the acid phase possesses an extremely high solubility for aromatic hydrocarbons. Quite a large amount of displacer can be added to the acid phase without apparently displacing any di-secondary alkylbenzene. By the use of very large amounts of displacer, it is possible to produce a second liquid phase which comprises displaced di-secondary alkylbenzene and displacer.

Since paraffinic hydrocarbons are soluble in the acid phase to only a relatively small extent, it is possible to wash from the acid phase-displacer solution the displaced secondary alkylbenzene. The wash hydrocarbon must be inert to the action of HF and BF_3 and non-reactive with the alkylbenzenes present in the acid phase. Benzene may be used as a wash hydrocarbon. It is preferred to use as the inert hydrocarbon a low boiling liquid paraffin such as propane, butane, pentane and hexane.

The wash hydrocarbon may be introduced into the acid phase-displacer solution simultaneously with the displacer, preferably as a single solution; or the wash hydrocarbon may be introduced into the acid phase after the addition of the displacer. In order to avoid rearrangement reactions, it is preferred to introduce the wash hydrocarbon substantially simultaneously after the introduction of the displacer.

It is preferred to carry out the displacement operation in a continuous countercurrent tower; in such an operation the acid phase is introduced in an upper portion of the tower, the displacer is introduced at a lower portion of the tower and the inert wash hydrocarbon is introduced at a point of the tower below the point of entry of the displacer.

The amount of inert wash hydrocarbon introduced must be enough to remove substantially all the displaced di-secondary alkylbenzene. In general, the amount of inert wash hydrocarbon used is between about 50 and 500 volume percent based on di-secondary alkylbenzene displaced, preferably between about 100 and 250 volume percent.

In order to avoid rearrangement reactions, the displacing zone should be operated at a temperature and for a contacting time such that essentially no rearrange-

ment reactions take place therein. Thus, the contacting time in the displacing zone and the temperature therein must be considered in determining the total contacting time to be utilized in the process.

Examples

The results obtainable by the invention are illustrated by several examples set out below. The runs were carried out using a carbon steel reactor provided with a 1725 R. P. M. stirrer. The order of addition of materials to the reactor was: (1) cumene or sec-butylbenzene of CP quality (2) commercial grade anhydrous liquid HF and (3) commercial grade BF_3 . The contents of the reactor were agitated during the addition of the HF and BF_3 ; the agitation was continued while the reactor was brought to the desired contacting temperature and maintained during the contacting time. All the runs were carried out under conditions such that only one liquid phase was present in the reactor at the completion of the run. The contents of the reactor were withdrawn into a vessel filled with crushed ice. An upper aqueous hydrocarbon layer formed above a lower aqueous layer. The hydrocarbon layer was decanted and washed with dilute ammonium hydroxide solution to remove HF and BF_3 . The neutral hydrocarbons were water washed to remove traces of ammonium hydroxide.

The hydrocarbons recovered from the reactor were fractionated in a laboratory distillation column provided with about 30 theoretical plates. Each product fraction was analyzed by a combination of boiling point, specific gravity, refractive index, and ultraviolet and infrared technique.

The results of these runs are set out in Table I.

Run 1 shows that cumene is almost completely converted at $+100^\circ\text{C}$. to a wide boiling range liquid product as well as large amounts of tar, probably condensed ring compounds, and gas.

Run 2, which was similar to run 1 in HF and BF_3 usage, shows that at $+51^\circ\text{C}$. the cumene disproportionated smoothly to form essentially pure meta diisopropylbenzene and 1,3,5-triisopropylbenzene. (In run 2—the tri-derivative was, within the error of the infrared method, the pure 1,3,5-isomer.) The long contacting time of 30 minutes at this temperature produced a product containing about 2 mols of the tri-derivative per mol of the di-derivative.

Run 3, which is like run 2 except for a lower temperature of $+14^\circ\text{C}$., gave a product wherein the ratio of di- to tri-derivatives is about 2, i. e., just the reverse of the distribution in run 2.

Run 4 was carried out at -20°C . and shows that, even with a 30 minute time, at this temperature no tri-derivative was formed. The di-derivative was virtually pure meta diisopropylbenzene.

Runs 5 and 6 were carried out to show the influence of time, at constant temperature, on the product distribution. In run 5, no tri-derivative was found, at a 5 minute contacting time at -5°C . contacting temperature. However, the 30 minute time in run 6 gave a significant yield of the tri-derivative. These runs indicate the need for coordinating both temperature and time in carrying out the process.

Run 7 was carried out with sec-butylbenzene. The product distribution in this run is substantially the same as the cumene in run 3. Infrared analysis of the tri-derivative indicated it to have the 1,3,5 orientation. This new compound 1,3,5-tri-secondary butylbenzene has the following physical characteristics:

Boiling point, $^\circ\text{C}$.	281 (760 mm.)
n_D^{20}	1.4825
d_4^{20}	0.853

TABLE I

Run No.	1	2	3	4	5	6	7
Charge:							
Cumene, mols.	5.1	2.5	2.5	2.5	2.5	2.5	1.5
Sec-butylbenzene, mols.							1.5
HF/sec-alkylbenzene, mol ratio	10.8	13.8	13.8	13.8	14.0	14.0	13.4
BF ₃ /sec-alkylbenzene, mol ratio	0.9	1.14	1.08	1.45	1.14	1.14	1.35
Temperature, °C.	+100	+61	+14	-20	-5	-5	+7
Time, Minutes	10	30	30	30	5	30	30
Reaction Product Mixture, mol percent:	(*)						
Benzene		58.0	53.3	47.5	47	48.1	54.0
Cumene		6.3	6.7	5.0	6	6.2	6.2
Sec-butylbenzene							6.2
M-Di-sec-alkylbenzene		13.0	26.7	47.3	47	42.3	25.4
Other-di-sec-alkylbenzene isomers		0.3	0.1	0.2	0	0	0
1,3,5-tri-sec-alkylbenzene		22.4	13.2	0	0	2.5	14.3
Other-tri-sec-alkylbenzene isomers		0	0	0	0	0	0
Higher boiling material		0	0	0	0	0	0
Sec-alkylbenzene conversion, percent	95	94	93	95	94	94	94
Portion going to di-derivative		28	57	100	100	92	56
Portion going to tri-derivative		72	43	0	0	8	44

* Weight basis: Propane, ca. 5%; benzene, 48%; Cumene, 5%; 198-218° C., 14%; 218-253° C., 14%; and tar, 15%.

ILLUSTRATIVE EMBODIMENT

The annexed figure, which forms a part of this specification, shows an illustrative embodiment of a method of carrying out the invention to produce essentially pure meta di-isopropylbenzene by disproportionating cumene. The figure is schematic and many items of equipment have been omitted, such as pumps, valves, etc., as these may be readily added thereto.

One thousand gals. a day of cumene feed from source 11 are passed by way of lines 12 and 13 into heat exchanger 14. From exchanger 14 the charge, consisting of the cumene, recycled isopropylbenzene, 50 gals. per day, and di-isopropylbenzene, 7 gals. per day, is passed by way of line 16 into line 17.

Anhydrous liquid hydrogen fluoride, 1360 gals./day (9 mols/mol of charge) is passed from line 26, through heat exchanger 27 and line 28 into line 17. Heat exchangers 14 and 27 lower the temperature of the charge and the liquid HF to a temperature of about -15° C. This temperature is about 5° C. lower than the desired reaction temperature of -10° C.

The contents of line 17 are introduced into mixer 31 which is provided with heat exchanger means 32. 3850 lbs. per day of BF₃ (0.9 mol/mol of charge) from line 29 is introduced into mixer 31. Mixer 31 is an apparatus able to rapidly intermingle the charge, liquid HF and BF₃. The heat exchanger means 32 withdraws the exothermic heat of formation of the complex and prevents the temperature at the discharge end of mixer 31 rising above -10° C.

An intimate mixture consisting of liquid HF, complex, hydrocarbons and BF₃ is discharged from mixer 31. About 100 p. s. i. g. of pressure are maintained on the system to keep the excess BF₃ in the liquid mixture. The liquid mixture is passed from mixer 31 by way of line 33 into reactor 34.

Reactor 34 is provided with heat exchanger means 36 and 37. To provide agitation and to insure the maintenance of a substantially uniform temperature of -10° C. throughout the reactor, reactor 34 is provided with baffles 38a, 38b and 38c and motor driven agitator 39.

Under these conditions, only one liquid phase exists at the outlet of reactor 34; an acid phase is withdrawn from the top of reactor 34 and is passed by way of line 41 into the upper portion of displacing zone 42. The reaction begins as soon as the HF, BF₃ and charge are mixed and continues until the meta di-isopropylbenzene is displaced from the complex. Therefore, the contacting time is measured as the time in mixer 31, reactor 34 and part of the total time in displacing zone 42. In this embodiment, a total time of about 30 minutes is utilized. Under these conditions no significant amount of tri-isopropylbenzene is formed.

Displacing zone 42 consists of a vertical vessel adapted for intimate contacting of two immiscible phases in a con-

tinuous countercurrent manner. (Other methods of contacting may be used.) In this embodiment, the displacer is 1,3,5-tri-isopropylbenzene which may be obtained from another operation but preferably is made by initially operating the process to produce 1,3,5-tri-isopropylbenzene as the predominant reaction product. 1,3,5-tri-isopropylbenzene from source 46 is passed by way of lines 47 and 48 into heat exchanger 49. Ordinarily sufficient displacer is made in the process to exceed the operational losses and "outside" displacer will be used only at the start-up of the process. The contents of line 48, i. e., "outside" and/or recycled tri-isopropylbenzene, are cooled in heat exchanger 49 to a temperature of -10° C. and are then introduced by way of line 51 into a lower intermediate portion of displacing zone 42. In this embodiment, 2230 gals./day of displacer are introduced into displacing zone 42, i. e., 2.6 mols per mol of di-isopropylbenzene introduced therein from line 41.

The very great solvent power of the liquid HF-complex solution for aromatic hydrocarbons, is overcome by adding hexane to the displacing zone. Hexane from source 53 is passed by way of valved line 54 and line 56 into heat exchanger 57. The contents of line 56, i. e., hexane from source 53 and recycled hexane are cooled in heat exchanger 57 to -10° C. and introduced by way of line 58 into a lower portion of displacing zone 42, at a point below the entry of displacer from line 51. In this embodiment, 1000 gals./day, i. e., 150 volume percent, of hexane, based on di-isopropylbenzene introduced from line 41, are introduced into displacing zone 42.

A raffinate phase is withdrawn overhead from zone 42. This consists essentially of hexane, benzene, cumene, meta di-isopropylbenzene, tri-isopropylbenzene and some slight amount of HF and BF₃. The raffinate phase is introduced by way of line 61 into fractionation zone 62. This zone 62 is shown schematically since one skilled in the distillation art can devise the proper method of separating the raffinate phase into a hexane fraction, also including the HF and BF₃; a benzene fraction, a cumene fraction, a product di-isopropylbenzene fraction and a displacer fraction.

A hexane fraction, which includes the HF and BF₃ present in the raffinate phase, is withdrawn and passed by way of lines 66 and 67 to line 56 for reuse in the displacing zone 42.

A benzene fraction is withdrawn from zone 62 by way of line 71, and is withdrawn from the process by way of valved line 74.

A product fraction, 660 gals./day, consisting essentially of meta di-isopropylbenzene is withdrawn from zone 62 by way of line 75 and passed to storage, not shown.

A cumene fraction is withdrawn from zone 62 and is recycled by way of lines 76 and 77, etc. to the reactor.

A bottoms fraction of tri-isopropylbenzene is withdrawn and recycled by way of lines 78 and 79 to line 48

for reuse in displacing zone 42. Some tri-isopropylbenzene is produced in the process; to maintain a constant ratio of displacer to isopropyltoluene introduced to the displacing zone, 6 gals./day of by-product 1,3,5-triisopropylbenzene are withdrawn from the process by way of valved line 81.

The extract (acid) phase is withdrawn from displacing zone 42 and is introduced by way of line 86 into decomposing zone 87. Decomposing zone 87 is provided with internal heater 88 and some fractionation means, not shown. The temperature of +20° C. in zone 87 is high enough to readily decompose the HF-BF₃ complexes but not high enough to cause the displacer to disproportionate or isomerize to any appreciable extent.

HF vapor and BF₃ gas are withdrawn from zone 87 and passed by way of line 91 into heat exchanger 92. In heat exchanger 92, the HF vapors are condensed and a liquid-gas stream is passed by way of line 93 into gas separator 94. BF₃ is withdrawn from gas separator 94 and is recycled by way of lines 96 and 29 to mixer 31. Make-up BF₃ is introduced from source 98 by way of valved line 99 into line 96. Liquid HF is recycled by way of lines 101 and 26. Make-up HF is introduced from source 102 by way of valved line 103 into line 101.

The bottoms fraction from decomposing zone 87 consists of hexane, benzene, cumene, di-isopropylbenzene and tri-isopropylbenzene. The bottoms fraction is withdrawn and introduced by way of line 106 into fractionation zone 107, shown schematically herein. A hexane fraction is withdrawn and recycled by way of lines 109, 67, etc. to displacing zone 42. A benzene fraction is withdrawn from the system by way of lines 111, 112 and 74. A bottoms fraction of tri-isopropylbenzene is withdrawn and recycled by way of lines 113 and 79, etc. to displacing zone 42. A cumene fraction is withdrawn and recycled to the reactor by way of lines 116, 77, etc.

As the conditions in decomposing zone 87 cause some back-isomerization of the meta di-isopropylbenzene to the ortho and para isomers, the mixed di-isopropylbenzene fraction from fractionation zone 107, 7 gals./day, is recycled by way of lines 117, 116, and 77, etc. to mixer 31. Or this fraction may be withdrawn from the system by way of valved line 117 and other lines not shown.

What is claimed is:

1. A disproportionation process which comprises contacting, under substantially anhydrous conditions, a charge consisting essentially of a single secondary alkylbenzene selected from the class consisting of mono-isopropylbenzene and mono-secondary butylbenzene, with at least about 0.5 mol of BF₃ per mol of secondary alkylbenzene charged and between about 3 and 50 mols of liquid HF to participate in complex-formation and to dissolve said charge under conditions to form a single essentially homogeneous liquid phase in said contacting zone, at a temperature between about -30° C. and about -5° C. wherein the permissible maximum time of contacting at about -5° C. is about 15 minutes and the lower the temperature of contacting the longer the corresponding permissible maximum contacting time to obtain the di-

secondary alkylbenzene as essentially the only disproportionation product, and removing the HF and BF₃ from the reaction product mixture under conditions which substantially avoid rearrangement reactions, thereby obtaining essentially pure 1,3 di-secondary alkylbenzene product fraction.

2. The process of claim 1 wherein the HF and BF₃ are removed by treating the acid phase with a cold reagent selected from the class consisting of water and aqueous alkaline solution.

3. The process of claim 1 wherein the HF and BF₃ are removed by rapid distillation at a temperature below about -5° C. such that essentially no rearrangement reaction takes place during said distillation procedure.

4. The process of claim 1 wherein said charge consists of mono-isopropylbenzene.

5. The process of claim 1 wherein said charge consists of mono-secondary butylbenzene.

6. The process of claim 1 wherein said acid phase is contacted with at least about 1 mol of a displacer per mol of di-secondary alkylbenzene present in said acid phase and substantially simultaneously thereafter with an amount of an inert liquid hydrocarbon sufficient to extract from said acid phase displaced di-secondary alkylbenzene, under conditions of temperature and time such that substantially no rearrangement reaction takes place, and separating a separate raffinate phase comprising inert hydrocarbon and di-secondary alkylbenzene from an acid phase comprising HF, BF₃, displacer and some di-secondary alkylbenzene, and recovering from said raffinate phase a di-secondary alkylbenzene comprising essentially the meta isomer, and wherein said displacer is a poly-alkylbenzene containing at least 3 alkyl groups that are selected from the class consisting of normal and secondary, which contain not more than 4 carbon atoms.

7. The process of claim 6 wherein said polyalkylbenzene is isodurene.

8. The process of claim 6 wherein said displacer is mesitylene.

9. The process of claim 6 wherein said displacer is 1,3,5-triisopropylbenzene.

10. The process of claim 6 wherein said displacer is 1,3,5-tri-secondary butylbenzene.

11. The process of claim 6 wherein said hydrocarbon is hexane.

12. The process of claim 6 wherein said hydrocarbon is pentane.

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