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RECOVERY OF PRIMARY NORMAL ALKYL BENZENES FROM MIXTURES CONTAINING THE SAME

Samuel H. Sharman, Berkeley, Calif., assignor to Chevron Research Company, a corporation of Delaware
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The present invention relates to a process for recovering monoalkyl benzenes having 8 to 16 carbon atoms in the alkyl groups, the alkyl groups being of normal or straight-chain structure and joined to the benzene nucleus predominantly in primary position.

Alkyl benzenes having 8 to 16 carbon atoms in the alkyl groups have long been known. Their use as intermediates in the manufacture of surface-active agents by sulfonation for the preparation of synthetic detergents has been widespread. Of these alkyl benzenes, the most outstanding and successful type has been the polypropylene benzenes, the sulfonates of which form the bulk of the synthetic detergents now commercially available. These are prepared by the alkylation of benzene, usually with hydrogen fluoride catalyst, as shown for example in U.S. Patent No. 2,477,382, followed by sulfonation, for example as shown in U.S. Patent No. 2,477,383. The polypropylene alkyl groups in the alkyl benzenes as thus prepared are of branched chain structure and are attached, for the most part, to the benzene nucleus through a secondary or tertiary carbon atom, i.e., one whose valence is satisfied by 4 or 3 other carbon atoms and with none or but one hydrogen atom.

While the polypropylene benzene sulfonates have enjoyed wide commercial success, and still form the bulk of synthetic detergents on the market, they are alleged to possess a serious disadvantage. Polypropylene sulfonates are asserted to resist breakdown or degradation, as by bacterial attack, into innocuous products. Remaining unchanged, they pollute water supplies, and interfere with sewage treating processes, for example, by causing undesired foaming. In other words, detergents produced from polypropylene benzenes are biologically hard materials, i.e., they resist the action of bacteria normally operative in similar environments in ingesting and breaking down organic material into less complex, harmless products. It is therefore desirable to be able to prepare synthetic detergents which are most amenable to decomposition, i.e., materials which are biologically soft, as a result of which they are readily broken down into harmless products.

It is also known that, in contrast to the polypropylene benzenes, certain other alkyl benzenes give rise to detergent materials which are biologically soft, i.e., are readily decomposed after use. Alkyl benzenes which are biologically soft have the alkyl group containing 8 to 16 carbon atoms in normal or straight-chain structure. And of these, particularly useful are the straight-chain primary alkyl benzenes in which the alkyl group is attached to the benzene nucleus through a primary carbon atom, i.e., one whose valence is satisfied by two carbon atoms and two hydrogen atoms. Primary normal alkyl benzenes of 8 to 16 carbon atoms in the alkyl groups are not only biologically soft, but also possess good foam properties, as shown for example in U.S. Patent No. 2,956,025. Normal secondary alkyl benzene sulfonates, although biologically soft, on the other hand, do not have the ability to improve the foam characteristics of detergent mixtures.

Primary normal alkyl benzenes convertible to the sulfonate having biological softness and good foam properties can be prepared by alkylating a benzene compound, such as benzene or toluene, with a straight-chain primary

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alkyl halide, such as dodecyl bromide. The process involves contacting the halide and benzene compound in the presence of anhydrous aluminum halide, such as aluminum bromide, at temperatures favoring the formation of the primary normal aromatic compound, for example, -40°C. to 10°C. While higher alkylation temperatures can be employed, the ratio of primary alkyl benzene to secondary alkyl benzene decreases, the higher alkylation temperatures tending to favor formation of secondary alkyl benzenes. For example, alkylation at -34°C. leads to a mixture containing approximately equal proportions of secondary alkyl benzenes and primary alkyl benzenes, whereas alkylation at 6°C. yields a mixture of 40% primary and 60% secondary alkyl benzenes. As indicated, the alkylation of benzene to produce primary and normal alkyl benzenes inevitably results in mixtures of primary normal alkyl and secondary alkyl benzenes, the proportions depending on reaction conditions.

It is therefore an object of the present invention to provide a process for the recovery of essentially pure $\text{C}_8\text{--C}_{16}$ normal primary alkyl benzenes from mixtures of primary and secondary alkyl benzenes.

The present invention is based on the discovery that substantially pure primary normal alkyl benzenes can be recovered from mixtures of the type hereinabove described by contacting said mixture with a catalyst agent comprising aluminum halide and hydrogen halide, such as aluminum chloride, aluminum bromide, hydrogen chloride, hydrogen bromide, and mixtures of these. Contacting is effected at temperatures and for a time such as to selectively dealkylate the secondary alkyl benzene component without substantially impairing the primary normal alkyl benzene component. The time of treatment is a function of the temperature, catalyst concentration, and catalyst type. Accordingly, as the temperature increases, the time necessary for dealkylation decreases, and as the catalyst concentration increases, the time of dealkylation decreases. Ordinarily, temperatures of the order of 0°C. to 35°C. will be found satisfactory. Temperatures as high as 80°C. can be employed, but then a very short contact time is required. Generally useful catalyst concentrations reside within the mol ratios of 0.1:1 to 3:1 aluminum halide to alkyl benzenes, and the aluminum halide to the hydrogen halide, in the range 1:1 to 1:100. The preferred catalyst is aluminum bromide because of its greater activity.

For economic reasons, it is generally preferred to operate at low catalyst concentrations. At a temperature of 0°C. to 35°C. using catalyst concentrations of the order specified, time of reaction will generally vary from 5 minutes to 24 hours. A satisfactory reaction time can be determined by analysis of the reaction mixture as the reaction proceeds, such as by the use of the analytical gas phase chromatography technique. This method analyzes aliquots of the reaction mixture for the various alkyl benzene components and the dealkylation products. Included is a saturated aliphatic hydrocarbon corresponding in carbon number to the alkyl group originally attached to the aromatic nucleus, as the main identifiable product. The analysis is carried out periodically and the reaction is stopped when the secondary benzenes have been converted, but short of any degradation of the primary alkyl benzene component.

While the reaction can be carried out in the absence of a diluent, in some instances the use of a diluent which is inert under the conditions of the reaction is advantageous. Examples of suitable diluents are the normally liquid hydrocarbons, aromatic and aliphatic, such as benzene, petroleum ether, or mixtures of these. The amount of diluent is not critical. Its function is to act as a diluent and/or as a solvent for the catalyst and the alkyl

benzenes. In general, proportions of diluent ranging, on a volume basis, from 1 to 50 for each volume of alkyl benzenes and catalyst are satisfactory.

Following reaction, the reaction mixture is treated to recover the desired primary normal alkyl benzene component. This is accomplished by quenching or stopping the reaction with aqueous acid in order to destroy the catalyst complex. At this stage, two phases are formed, a lower aqueous phase and an upper hydrocarbon phase rich in primary alkyl normal benzene content. In order to facilitate phase formation, it may sometimes be advantageous to add an organic liquid, such as a low boiling petroleum ether, to dissolve the alkyl benzene. The phases can be separated simply by drawing off the lower aqueous phase. The organic phase is washed with an aqueous solution of a weak base, such as sodium bicarbonate, to neutralize any residual acid entrained in this layer, followed by washing with water to remove inorganic materials. The water-washed material is then dried, such as over a dehydrating agent, for example, calcium sulfate. Finally, the desired alkyl benzene is isolated as a bottoms product after distillation removal of the low boiling hydrocarbons, including benzenes and petroleum ether, and alkanes formed by dealkylation.

In the following examples, all parts are on a weight basis.

EXAMPLE 1

(a) Preparation of a mixture of primary and secondary dodecylbenzenes

Benzene, 1 liter was placed in a 2-liter, three-necked flask fitted with a mechanical stirrer, a thermometer, and an adding funnel. The system was protected from moisture using a drying tube containing calcium sulfate. After cooling to 6° C., 7.25 grams of purified aluminum bromide was added by rapid mechanical transfer from the weighing vial to the reaction flask. The mixture was stirred an additional 2-5 minutes during which time the aluminum bromide dissolved, giving a very light yellow solution. A solution of 100 grams freshly silica-treated n-dodecyl bromide in 300 ml. benzene was then added dropwise over a period of about five minutes to the stirred solution of catalyst. The alkyl bromide solution was precooled to about 6° C. to minimize local heating during reaction. The reaction temperature was maintained between 6° C. and 8° C. by control of addition rate. Upon addition of the first few drops of bromide solution, the color of the reaction mixture changed to a medium yellow-orange.

After 30 minutes the contents of the reaction flask were worked up as follows: Hydrochloric acid, 3 N, in an amount of 1500 ml. was added to the reaction mixture while agitating it. About 500 ml. of pentane was then added, and agitation continued for 15 minutes. Upon standing, two phases formed, a lower aqueous phase, and an upper organic phase. This latter phase was isolated and was washed once with one liter of 5% NaHCO₃, twice with one liter of water, and then dried over calcium sulfate. The dried material was distilled under vacuum to remove the low boiling components, mainly pentane, benzene, and dodecane, and the dodecyl benzenes were taken overhead (bottoms product 118-159° C./2 mm.). As a result of this work-up, there was obtained 86.9 grams of mixed dodecyl-benzenes. The over-all yield was 88% (mol). Analysis of the mixture by vapor phase chromatography showed that the mixture contained 37.1% 1-phenyl dodecane and 62.9% secondary dodecylbenzenes.

(b) Dealkylation of secondary dodecylbenzenes

In a round bottom three-necked flask equipped with a mechanical stirrer, a thermometer, an adding funnel, a reflux condenser, and a gas inlet tube, and protected from moisture by a drying tube filled with calcium sul-

fate, there were placed: benzene, 29.0 parts, and 1.738 parts of the mixture of dodecylbenzenes prepared above. Then 1.08 parts of Al₂Br₆ were added. About 1 liter of gaseous HBr was bubbled through the solution during about 2 minutes at the beginning and again after 45 minutes. The temperature was maintained at 25° C. throughout the additions and the reaction period. Samples were removed at 3, 11, and 100 minutes after adding all of the Al₂Br₆. These were worked up and analyzed as in (a). The three samples showed 49.4%, 69.2%, and 100% 1-phenyl dodecane, respectively. The corresponding amounts of secondary dodecylbenzenes were 50.6%, 30.8%, and 0%, respectively.

The work-up of each of the analytical samples was carried out as follows: The acid solution in the separatory funnel was vigorously shaken, and then 25 ml. of pentane was added and the shaking continued for a short time. After settling, the organic layer was isolated, washed once with 5% sodium bicarbonate, and twice with water. Thereafter, it was dried for three hours over calcium sulfate. The bulk of the solvent was then boiled off on a steam plate, and the remaining solution was subjected to a vapor phase chromatographic analysis. Before the bicarbonate wash, 200 microliters of n-hexadecane was added to provide an internal standard for yield determination.

EXAMPLE 2

In this example, the mixture of dodecylbenzenes is prepared and then dealkylated without isolating the mixture. The catalyst for dealkylation is the same Al₂Br₆ used for alkylation, plus the HBr liberated during alkylation. Because alkylation was effected at 6° C., the same isomeric ratio is formed initially as in Example 1(a), i.e., about 41% primary and 59% secondary dodecylbenzenes.

In a 100 ml. flask fitted with a magnetic stirrer, a dropping funnel, and protected by a drying tube, were placed 50 ml. benzene and 14.798 grams aluminum bromide. After cooling to 3° C., 5.006 grams n-dodecylbromide in 24 ml. benzene were added over a period of three minutes. An initial heat evolution was observed, the temperature rising to a maximum of 9° C. Shortly after addition was complete, the temperature returned to and was maintained between 3° C. and 6° C. Small aliquots were withdrawn at 1, 14, and 90 minutes after all the bromide had been added. These samples were treated as in Example 1(a) and analyzed by vapor phase chromatography. It was found that the percentage of primary dodecylbenzene was 47.3%, 54.9%, and 100%, respectively, for the three samples. At the same time intervals, the secondary dodecylbenzenes concentration was 52.7%, 45.1%, and 0%.

EXAMPLE 3

This example illustrates the adverse effect of too high a temperature. The reaction mixture of Example 2 after 90 minutes, which contained only primary dodecylbenzenes and dealkylation products, was heated to 25° C. After 24 hours at this temperature, no dodecylbenzene remained.

EXAMPLE 4

Dealkylation of secondary octyl benzenes

To the apparatus of Example 1(b) there was charged 26.4 parts of benzene and 5.07 parts of mixed octyl benzenes (39.8% primary and 60.2% secondary). This solution was held at 25° C. as 3.56 parts of Al₂Br₆ were added. Two minutes after the addition of the aluminum bromide, gaseous HBr was bubbled in for an additional two minutes in order to saturate the solution. Samples were removed at 3 minutes, 15 minutes, 1 hour 53 minutes, and at 3 hours 26 minutes after saturation. The percent primary octyl benzene in each of these samples was as follows: 59.5; 73; 83.8; and 91.8, respectively. Additional time would be required to complete the dealkylation.

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EXAMPLE 5

Dealkylation of secondary hexyl benzenes

A mixture of hexyl benzenes containing 34% primary hexyl benzenes and 66% secondary hexyl benzenes was

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20 ml. of benzene was added over a period of 1½ minutes. Samples were removed and analyzed as described previously, the time being measured from the complete addition of the alkyl bromide. The following results were obtained:

Sample No.	Time Min.	Relative Amounts of Dodecylbenzenes, Percent				Dodecane, Mol Percent
		1-phenyl	2-phenyl	3-phenyl	4-, 5-, and 6-phenyl	
1-----	1	35.1	19.9	12.9	32.1	12.3
2-----	8	51.7	15.0	10.0	23.3	36.9
3-----	22	62.5	10.6	7.6	19.3	48.6
4-----	53	67.7	8.7	6.7	16.9	52.5
5-----	1,200	71.0	8.0	5.0	16.0	56.8

prepared. Benzene, 32.5 parts, and 1.148 parts of the above-described mixture of hexyl benzenes were placed in a round bottom flask fitted with a gas dispersion tube, magnetic stirrer, and protected by a drying tube. By rapid mechanical transfer, 1.200 parts aluminum bromide was added. The temperature was maintained at 25° C. Approximately 2 parts of anhydrous hydrogen bromide was bubbled through the liquid mixture immediately after addition of Al_2Br_6 , and subsequently every 45 minutes similar amounts were added. Samples were withdrawn periodically for analysis. These samples were treated and analyzed as described in Example 1(a). The following results were obtained:

	Starting Material	Time After Addition of Al_2Br_6			
		3 Min.	11 Min.	100 Min.	180 Min.
1-phenyl hexane...	34.0	48.4	58.2	91.0	97.0
2-, and 3-phenyl hexane-----	66.0	51.6	41.8	9.0	3.0

Further treating time would give a pure 1-phenyl hexane.

EXAMPLE 6

This example shows that secondary alkyl benzenes can be dealkylated without material dealkylation of the primary alkyl benzenes. A mixture of dodecylbenzenes was prepared in the following manner. Benzene, 150 ml., was placed in an apparatus similar to that of Example 1(a) and was maintained at 35° C. throughout the experiment. To this benzene there was added 5.43 grams of Al_2Br_6 . Then 12.5 g. of n-dodecylbromide in

Additional time would be required to complete the dealkylation of the secondary dodecylbenzenes. However, based on these values, it is possible to prove that substantially no dealkylation of the primary alkyl benzene has occurred.

I claim:

Process for increasing the recoverable content of a primary normal C_8 - C_{16} monoalkyl benzene from a mixture of secondary and primary normal monoalkyl benzene components having 8 to 16 carbon atoms in the alkyl groups, which comprises contacting said mixture at a temperature in the range 0° C. to 35° C. with aluminum bromide and hydrogen bromide for a time selectively to dealkylate the secondary alkyl benzene component of said mixture and convert the secondary alkyl group to alkane, while leaving the primary alkyl benzene component substantially unimpaired, and recovering said primary normal monoalkyl benzene component.

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DELBERT E. GANTZ, *Primary Examiner*.

ALPHONSO D. SULLIVAN, *Examiner*.