Patented Dec. 9, 1947 2,432,381

UNITED STATES PATENT OFFICE

2,432,381

PREPARATION OF ALKYL-SUBSTITUTED AROMATIC HYDROCARBONS

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No Drawing. Application November 28, 1945, Serial No. 631,470

17 Claims. (Cl. 260—671)

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This invention relates to novel aromatic compounds, and mixtures thereof, containing alkyl substitutents, and to a process for the manufacture of such products. More particularly the present invention is directed to a novel process for the preparation of alkyl-substituted aromatic hydrocarbons, especially long-chain alkyl-substituted toluenes, xylenes, ethylbenzenes, propylbenzenes, butylbenzenes, etc.

Heretofore long-chain alkyl-substituted benzenes have been prepared by methods known to the art, such as by condensing benzene with chlorinated paraffins through the agency of metal halide-type catalysts. The use of halogen compounds adds materially to the cost of these products. Other compounds which have been employed for the introduction of long-chain alkyl groups into aromatic hydrocarbons, according to the prior art, include long-chain alcohols and long-chain olefins, but the use of these reactants has been limited because of their relatively high cost.

An object of this invention is to provide novel and useful alkyl-substituted aromatic hydrocarbons. A further object is to provide a direct and economical method for preparing these hydrocarbons. Other objects of the invention appear hereinafter.

This invention comprises the introduction of long-chain alkyl groups into short-chain alkyl-substituted aromatic hydrocarbons by heating ethylene with a short-chain alkyl-substituted aromatic hydrocarbon, under suitable conditions of temperature and pressure, in the presence of a catalytic quantity of a ketaldone derivative containing the group >C=N—. At a temperature of 200° to 300° C. and under a pressure of at least 400 atmospheres, the desired reaction proceeds at a very convenient rate. The products may be regarded as having the structure, $H(HC_2CH_2)_nR$, wherein n is an integer, and R is the monovalent hydrocarbon radical derived from said short-chain alkyl-substituted aromatic hydrocarbon by removal of a single hydrogen atom. In specific embodiments, n may have average values of from about 7 to about 50, while individual molecules may be present in which n is no greater than 2 or 3. The reaction which occurs may be illustrated by the equation

$$HR+nCH_2CH_2 \rightarrow H(CH_2CH_2)_nR$$

in which the symbols n and R have the significance given above.

By short-chain alkyl-substituted aromatic hydrocarbon is meant aromatic hydrocarbons in

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which the alkyl substituent is of less than 6 carbon atoms in chain length.

In carrying out the process of the present invention, it is desirable to operate under superatmospheric pressure. The apparatus requirements, therefore, preferably comprise means for heating and agitating such vessels, and appropriate connecting lines, gages, controlling valves, and the like. Preferably means are also provided for deoxygenating the ethylene. If desired, suitable pumps or injectors may be provided for adding solutions or suspensions of the catalyst or additional arcmatic hydrocarbon to the reactor. For continuous types of reactors, which may assume any of various forms, suitable pumps and metering devices are provided.

The reactants employed in practicing this invention comprise ethylene, a short-chain alkyl-substituted aromatic hydrocarbon, and, as catalyst, a compound which contains the group >C=N— and is derived from a ketaldone. The reactants may be brought into mutual contact in a reaction zone in any order of addition and may be preheated or not, separately or mixed, before their respective additions to the reaction zone. It is generally inadvisable to permit the catalyst to be subjected to elevated temperatures more than momentarily before entering the reaction zone. The process may be operated batchwise, continuously or semi-continuously. The following detailed description illustrates one manner of carrying out the batchwise operation of the process.

A pressure-resistant reaction vessel is charged with a short-chain alkyl-substituted aromatic hydrocarbon and catalyst. This charging operation is preferably carried out after purging the reaction vessel of air with deoxygenated nitrogen or other inert gas. In order to prevent entrance of air, the charging is usually conducted under a blanket of inert gas. Alternatively, the reaction charge can be sucked into the closed and evacuated reaction vessel by use of a loading lock. The vessel is then closed, evacuated, placed in a shaker provided with a heater and connected to a reservoir of ethylene. Controlling and recording thermocouples are placed in position, the vessel pressured with ethylene and heating and agitation are started. On reaching the selected reaction temperature, the reaction begins, usually without the induction period which is commonly observed in polymerization reactions. The course of the reaction may be followed by the pressure drop due to the utilization of ethylene. The pressure may be maintained in the desired range by

any of several means such as by addition of ethylene from high pressure storage, by injecting short-chain alkyl-substituted aromatic hydrocarbon, or by injecting a mixture of ethylene and short-chain alkyl-substituted aromatic hydrocarbon. At the end point of the reaction, which is marked by cessation of pressure drop, the vessel is cooled, bled of excess ethylene, opened and the reaction mixture discharged. The product may be isolated by procedures illustrated in the examples, or by simple modifications thereof readily apparent to one skilled in the art.

In the following examples, reactions were carried out in a 400 cc. reaction vessel. Parts are by weight unless otherwise stated.

Example 1.—A silver-lined high-pressure reaction vessel is charged with 200 parts of cumene and 0.2 part of benzalazine. The vessel is evacuated, pressured with ethylene (approximate weight ratio, ethylene:cumene=0.25), and heating and agitation are started. During a reaction time of 14 hours, throughout which the temperature is maintained at 248° to 250° C. and the pressure at 850 to 1000 atmospheres, there is a total observed pressure drop of 1330 atmospheres. The vessel is then cooled, bled of excess ethylene, opened and the contents discharged. The crude reaction mixture is submitted to steam distillation to remove unreacted cumene. By this means there is obtained 69 parts of a soft, buff-colored wax. This ethylene/cumene wax contains 86.22% carbon, 13.57% hydrogen, and has an average molecular weight (determined ebullioscopically) of 889. The infrared absorption spectrum of the wax, compared with the infrared absorption spectra of cumene and of polyethylene, shows that the new product absorbs strongly at wave-lengths characteristic of the aromatic C—H group, namely, at 3.23 microns, 3.25 microns, and 3.29 microns, as well as in the region above 3.3 microns which is characteristic of aliphatic CH_2 groups. As estimated from the relative intensities of absorption in these characteristic regions, the wax appears to contain approximately 20% as much absorbing aromatic C—H as does cumene, which corresponds to an ethylene/cumene ratio of about 15. It is to be understood, of course, that this figure may be in error by as much as several units, due to the difficulties inherent in the method.

That the ethylene/cumene product is not a physical mixture of cumene and polymerized ethylene can be demonstrated by distillation of the product under low pressure. An ethylene/cumene sample, prepared as above, was evacuated for 16 hours in a steam bath at 20 mm. pressure, to remove traces of cumene left after steam distillation. The product was then distilled in a short path still at 0.01 mm. pressure. A foreshot (1) boiling up to approximately 56° C. was taken. The next fractions were taken as follows:

(2) 56°–154° C. at 0.01 mm.
(3) 154°–202° C. at 0.01 mm.
(4) 202°–226° C. at 0.01 mm.

All of these showed strong infrared absorption bands at 3.23, 3.25, 3.29μ respectively as well as strong general absorption in the region above 3.3μ characteristic of the aliphatic CH_2 group. This indicates that the cumene and ethylene are chemically combined.

Similar ethylene/cumene waxes are obtained when the above experiment is repeated using the following catalysts: acetone oxime, benzaldehyde phenylhydrazone, cyclohexanone semicarbazone, benzalaniline, and isobutyraldehyde anil.

The waxy product obtained as described above is converted to a detergent by sulfonating 19 parts of the wax, dissolved in 50 parts by volume of carbon tetrachloride, with 3.6 parts of chlorosulfonic acid. The sulfonation is accelerated by strong illumination from a 300 watt, clear Mazda lamp located at a distance of 3 inches from the glass reactor. After 3 hours the reaction mixture is poured onto water-ice mixture containing sufficient sodium hydroxide to neutralize all acid. The carbon tetrachloride is removed by evaporation on the steam bath and the residue is diluted with water and filtered. The filtrate is concentrated by evaporation to separate the sodium salt of sulfonated ethylene/cumene. Aqueous solutions of this sodium sulfonate do not form a precipitate when treated with aqueous solutions of calcium or magnesium salts. This behavior indicates that the sulfonate group entered the molecule on the aromatic ring. Aqueous solutions of the sodium sulfonate of ethylene/cumene foam strongly, wet sulfur and deterge soiled fabric. The dried sodium sulfonate contains 10.45% sulfur.

The long-chain alkyl-substituted aromatic hydrocarbon prepared as above described can also be sulfonated by a variety of other means. For example, sulfuric acid, fuming sulfuric acid, sulfuric anhydride, or certain SO_3 addition products with ethers may be used as sulfonating agent in place of the above-described chlorosulfonic acid. Light-colored sulfonation products can be prepared by sulfonating with relatively dilute acid for extended reaction times. For example, sulfonation by means of a large excess of 92 to 96% sulfuric acid at 40° C. to 50° C. for several hours gives fairly complete reaction with little if any darkening. When fuming sulfuric acid is used it is necessary to restrict the excess to the minimum required for complete reaction and to maintain a relatively low temperature. Fuming acids, containing up to 20% free sulfuric anhydride, may be conveniently employed at temperatures ranging from −20° C. to +10° C. Low temperatures are readily maintained by the use of a low boiling solvent for the ethylene products described and for this purpose it may be found suitable to use sulfur dioxide. In order to force the sulfonation to completion, while yet maintaining low reaction temperatures, it is sometimes desirable to conduct the sulfonation in the presence of such water binding agents as phosphoric anhydride, acetic anhydride, acetyl chloride, or other acid chlorides.

Example 2.—A silver-lined high-pressure reaction vessel is charged with 200 parts of toluene and 0.2 part of benzalazine. The vessel is closed, evacuated, and pressured with ethylene, the weight ratio of ethylene:toluene being about 0.2. During a reaction time of 8.75 hours, throughout which the temperature is maintained at 249° to 251° C. and the pressure at 505 to 600 atmospheres. The vessel is then cooled, bled of excess ethylene, opened and the contents discharged. The product is isolated as in Example 1 and amounts to 23 parts. This is an ethylene/toluene wax having an average molecular weight of 369 (ebullioscopic).

A product prepared as described above was distilled in a short-path still at 0.01 mm. pressure. The fractions have the properties summarized below in Table I.

TABLE I

Properties of distilled ethylene/toluene product

Fraction	Boiling Pt. (° C. at 0.01 mm. Hg)	Per cent toluene by weight [1]	Av. mol. wt.[2] (apparent, from infrared spectra)
(1) (Toluene)			
(2)	46–127	47	196
(3)	97–144	39.5	233
(4)	144–188	45	204
(5)	189–191	35	263
(6)	196–212	32	288
(7)	212–220	32	288
(8)	232–240	23	400

[1] Calculated from infrared absorption. The average intensities of the 3.23μ and 3.25μ bands were taken since they were less influenced by CH_2 absorption than was the 3.29μ band.

[2] The values above are based on the assumed retention of toluene's five aromatic CH groups by the product. The other equally possible configuration wherein the ethylene chain is linked to one of the nuclear carbons will give apparent molecular weights equal to 80% of the above figures.

These data plus the fact that the infrared absorption spectra show strong general absorption in the region characteristic of aliphatic CH_2 groups, indicate that ethylene and toluene are chemically combined by the reaction described.

Example 3.—A stainless steel-lined high-pressure reaction vessel is charged with 200 parts of toluene and 0.4 part of acetone oxime. The vessel is evacuated and pressured with ethylene, the weight ratio of ethylene:toluene being about 0.25. During a reaction time of 14.25 hours, throughout which the temperature is maintained at 247° to 250° C. and the pressure at 690 to 980 atmospheres, there is a total observed pressure drop of 895 atmospheres. This reaction mixture, worked up as in Example 1, yields 60 parts of an ethylene/toluene wax having an average molecular weight of 656 (determined ebullioscopically).

Example 4.—Example 3 is repeated using ethylbenzene in place of toluene. A waxy ethylene/-ethylbenzene reaction product is obtained.

The short chain alkyl-substituted aromatic hydrocarbon which is employed as a reactant in the process of this invention may be any of the short chain mono- or polyalkyl aromatic hydrocarbons. Preferably short chain monoalkyl-substituted aromatic hydrocarbons containing from seven to eleven carbon atoms are employed. Specific compounds coming within this preferred group include toluene, ethylbenzene, n-propylbenzene, isopropylbenzene (cumene), the butyl- and amylbenzenes, and α- and β- methylnaphthalenes. Polyalkylbenzenes are less preferred and those employed preferably should contain a total of not more than five carbon atoms in the alkyl substituents.

The ethylene used in the practice of this invention may contain small amounts of ethane, propane, nitrogen, hydrogen, carbon dioxide or oxygen. Oxygen in concentrations above 1000 ppm. generally operates to the detriment of the reaction. Consequently ethylene purified to contain less than 100 ppm., generally less than 50 ppm. and preferably less than 10 ppm. of oxygen is employed. Ethylene may be conveniently purified by suitable scrubbing, by catalytic removal of the impurities or by distillation.

The initial weight ratio of ethylene to aromatic hydrocarbon hereafter called weight ratio of reactants, should be not greater than 1, if excessive independent polymerization of the ethylene is to be suppressed. To accomplish these

desired results, there must be a weight excess of the aromatic hydrocarbon over the ethylene despite the apparent requirement for an excess of ethylene as judged by the empirical equation previously given. The weight ratio of reactants is conveniently of the order of 0.25 for batch operation but may be as low as 0.07, while higher ratios, for example, up to 0.9 are suitable. In continuous operation, even lower ratios, for example, as low as 0.02, may be practically employed. Generally the lower the weight ratio of reactants the lower the average molecular weight of the product.

As catalyst for inducing the reaction of this invention there may be used any compound which contains the group >C=N— and which is derived from a ketaldone, i. e., a ketone or aldehyde. Specific catalysts useful in the practice of this invention include azines (containing the group >C=N—N=C<) such as benzalazine, heptaldazine and diphenylketazine; oximes (containing the group >C=NOH) such as d-camphor oxime, acetone oxime, alpha-benzil dioxime, butyraldoxime, alpha-benzoin oxime, dimethylglyoxime; hydrazones (containing the group >C=N—N<) such as benzaldehyde phenylhydrazone, phenylhydrazones of cyclohexanone, cyclopentanone, acetophenone, menthone, camphor, and benzophenone; semicarbazones (containing the group >C=N—NHCONH$_2$) such as semicarbazones of acetone, methyl ethyl ketone, diethyl ketone, biacetyl, cyclopentanone, cyclohexanone, acetophenone, propiophenone, camphor, and benzophenone, Schiff's bases (containing the group >C=N—) such as benzalaniline, benzal-p-toluidine, benzal-o-toluidine, benzaldehyde derivatives of methylamine, ethylamine, and heptylamine; anils and analogous compounds of other amines, such as acetaldehyde anil, acetone anil, isobutyraldehyde anil, n-butyraldehyde anil, heptaldehyde anil, etc. These catalysts are generally used in amounts from about 0.001% to 0.5% by weight based on the total reactants. While it is generally not necessary, for attaining extremely high rates of reaction or for other special purposes, even higher amounts of catalysts may be used; for example, amounts ranging up to as high as 1% or even 5% as an upper limit can be employed. For their best utility in the practice of this invention, the foregoing catalysts should be highly purified. For example, some of the phenylhydrazones and some of the Schiff's bases are relatively unstable and decompose on exposure to moisture or air. When the catalysts show such sensitivity they should be prepared immediately before use. Some, such as benzalaniline, can be satisfactorily stored in a vacuum or under a nitrogen atmosphere.

The temperatures and pressures employed in the practice of this invention are interdependent variables and each must be determined with relation to the other. Generally temperatures in the range of 200° to 300° C. and pressures in the range of 400 to 1500 atmospheres are employed. The use of higher temperatures generally makes possible the use of lower reaction pressures and conversely lower reaction temperatures make necessary an increase in the reaction pressure. Somewhat higher pressures, for example, up to 3,000 atms. or more may be employed and are particularly desirable for high rates of reaction. When operating in a continuous manner, the time of contact influences the reaction temperature and the operable range given must be extended to about 400° C. particularly for short contact times.

In general, increase in reaction temperature makes for a decrease in the average molecular weight of the product while an increase in pressure increases the average molecular weight.

The equipment used in the practice of this invention should be strong enough to withstand the temperatures and pressures encountered. Those portions of the apparatus which come in contact with the reactants are constructed of noncatalytic materials and should be of a type which does not induce side reactions. Such materials may be stainless steel, silver, tin, lead, enamel, and glass.

It is preferable to agitate the reactants, i. e., any means may be employed for intimately mixing the reactants such as by stirring, atomization, bubbling the gas phase through the liquid phase of the reaction, by turbulent flow in a tubular reactor, and the like.

Although batch operations have been described herein, the process of this invention can be easily carried out in a continuous manner in either tubular or autoclave reactors. Continuous operation offers numerous advantages in control of temperature, high space-time yield and increased flexibility in the reactant concentrations that may be employed.

The products of this invention may be employed as lubricants, as additives for lubricating oils and greases, and as raw materials for conversion to a wide variety of useful products. Of particular importance are the sulfonated products which are valuable as detergents in hard water and sea water because of the solubility of their alkaline earth metal salts. Various salts of the sulfonated products are also useful in wetting, emulsification and other surface active applications. Nitration and chlorination can also be controlled to give mainly nuclear substitution and these products are useful respectively for reduction to valuable long-chain amines and hydrolysis to bactericidal and bacteriostatic phenols.

The present invention involves the discovery that the >C=N— compounds disclosed herein are excellent alkylation catalysts. In its broadest aspect the invention therefore contemplates the alkylation of various hydrocarbons (isoparaffins, etc.), and other organic compounds, containing a reactive C—H bond, by means of an olefin in the presence of the said alkylation catalyst.

We claim:

1. A process for the alkylation of short chain alkyl-substituted aromatic hydrocarbons which comprises reacting the said alkyl-substituted aromatic hydrocarbon with ethylene in the presence of a catalyst containing the >C=N— grouping, said catalyst being selected from the class consisting of the oximes, hydrazones, azines, semicarbazones, Schiff's bases, and anils of ketaldones.

2. A process for the alkylation of short chain alkyl-substituted aromatic hydrocarbons which comprises reacting the said alkyl-substituted aromatic hydrocarbon with ethylene, the initial weight ratio of ethylene:aromatic hydrocarbon being not greater than 1:1, in the presence of a catalyst containing the >C=N— grouping, said catalyst being selected from the class consisting of the oximes, hydrazones, azines, semicarbazones, Schiff's bases, and anils of ketaldones.

3. A process for the alkylation of short chain alkyl-substituted aromatic hydrocarbons which comprises reacting cumene with ethylene, the initial weight ratio of ethylene:cumene being not greater than 1:1 in the presence of a catalyst containing the >C=N— grouping, said catalyst being selected from the class consisting of the oximes, hydrazones, azines, semicarbazones, Schiff's bases, and anils of ketaldones.

4. A process for the alkylation of toluene which comprises reacting toluene with ethylene, the initial weight ratio of ethylene:toluene being not greater than 1:1 in the presence of a catalyst containing the >C=N—grouping, said catalyst being selected from the class consisting of the oximes, hydrazones, azines, semicarbazones, Schiff's bases, and anils of ketaldones.

5. A process for the alkylation of ethylbenzene which comprises reacting ethylbenzene with ethylene, the initial weight ratio of ethylene:ethylbenzene being not greater than 1:1, in the presence of a catalyst containing the >C=N— grouping, said catalyst being selected from the class consisting of the oximes, hydrazones, azines, semicarbazones, Schiff's bases, and anils of ketaldones.

6. A process for the alkylation of short chain alkyl-substituted aromatic hydrocarbons which comprises reacting the said alkyl-substituted aromatic hydrocarbon with ethylene in the presence of a catalytic quantity of acetone oxime.

7. A process for the alkylation of short chain alkyl-substituted aromatic hydrocarbons which comprises reacting the said alkyl substituted aromatic hydrocarbon with ethylene in the presence of a catalytic quantity of benzalazine.

8. A process for the alkylation of short chain alkyl-substituted aromatic hydrocarbons which comprises reacting the said alkyl-substituted aromatic hydrocarbon with ethylene in the presence of a catalyst containing the >C=N— grouping, said catalyst being selected from the class consisting of the oximes, hydrazones, azines, semicarbazones, Schiff's bases, and anils of ketaldones, at a temperature in the range of about 200° to 300° C., under a pressure in the range of 400 to 1500 atmospheres, whereby a waxy alkyl-substituted aromatic hydrocarbon is formed, and thereafter separating the said waxy alkyl-substituted aromatic hydrocarbon from the resultant mixture.

9. A process for the alkylation of short chain alkyl-substituted aromatic hydrocarbons which comprises reacting the said alkyl-substituted aromatic hydrocarbon with ethylene, the initial weight ratio of ethylene:aromatic hydrocarbon being not greater than 1:1, in the presence of a catalyst containing the >C=N— grouping, said catalyst being selected from the class consisting of the oximes, hydrazones, azines, semicarbazones, Schiff's bases, and anils of ketaldones at a temperature in the range of about 200° to 300° C., under a pressure in the range of 400 to 1500 atmospheres, whereby a waxy alkyl-substituted aromatic hydrocarbon is formed, and thereafter separating the said waxy alkyl-substituted aromatic hydrocarbon from the resultant mixture.

10. A process for the alkylation of short chain alkyl-substituted aromatic hydrocarbons which comprises reacting cumene with ethylene, the initial weight ratio of ethylene:cumene being not greater than 1:1, in the presence of a catalyst containing the >C=N— grouping, said catalyst being selected from the class consisting of the oximes, hydrazones, azines, semicarbazones, Schiff's bases, and anils of ketaldones, at a temperature in the range of about 200° to 300° C., under a pressure in the range of 400 to 1500 atmospheres, whereby a waxy alkyl-substituted aromatic hydrocarbon is formed, and thereafter separating the said waxy alkyl substituted aromatic hydrocarbon from the resultant mixture.

11. A process for the alkylation of short chain

alkyl-substituted aromatic hydrocarbons which comprises reacting toluene with ethylene, the initial weight ratio of ethylene:toluene being not greater than 1:1 in the presence of a catalyst containing the >C=N— grouping, said catalyst being selected from the class consisting of the oximes, hydrazones, azines, semicarbazones, Schiff's bases, and anils of ketaldones, at a temperature in the range of about 200° to 300° C., under a pressure in the range of 400 to 1500 atmospheres, whereby a waxy alkyl-substituted aromatic hydrocarbon is formed, and thereafter separating the said waxy alkyl-substituted aromatic hydrocarbon from the resultant mixture.

12. A process for the alkylation of short chain alkyl-substituted aromatic hydrocarbons which comprises reacting ethylbenzene with ethylene, the initial weight ratio of ethylene:ethylbenzene being not greater than 1:1, in the presence of a catalyst containing the >C=N— grouping, said catalyst being selected from the class consisting of the oximes, hydrazones, azines, semicarbazones, Schiff's bases, and anils of ketaldones, at a temperature in the range of about 200° to 300° C., under a pressure in the range of 400 to 1500 atmospheres, whereby a waxy alkyl-substituted aromatic hydrocarbon is formed, and thereafter separating the said waxy product from the resultant mixture.

13. A process for the alkylation of short chain alkyl-substituted aromatic hydrocarbons which comprises reacting the said alkyl-substituted aromatic hydrocarbon with ethylene in the presence of a catalytic quantity of acetone oxime, at a temperature in the range of about 200° to 300° C., under a pressure in the range of 400 to 1500 atmospheres, whereby a waxy alkyl-substituted aromatic hydrocarbon is formed, and thereafter separating the said waxy alkyl-substituted aromatic hydrocarbon from the resultant mixture.

14. A process for the alkylation of short chain alkyl-substituted aromatic hydrocarbons which comprises reacting the said alkyl-substituted aromatic hydrocarbon with ethylene in the presence of a catalytic quantity of benzalazine, at a temperature in the range of about 200° to 300° C., under a pressure in the range of 400 to 1500 atmospheres, whereby a waxy alkyl-substituted aromatic hydrocarbon is formed, and thereafter separating the said waxy alkyl-substituted aromatic hydrocarbon from the resultant mixture.

15. A process for the synthesis of a waxy long chain alkyl-substituted cumene derivative which comprises heating about 200 parts by weight of cumene with about 0.2 part of benzalazine at a temperature of about 248° to 250° C. in a closed vessel containing ethylene under a pressure in the range of 850 to 1000 atmospheres, the weight ratio of ethylene:cumene being about 0.25, whereby a waxy alkyl-substituted cumene is formed, and thereafter separating the said waxy product from the resultant mixture.

16. A process for the synthesis of a waxy long chain alkyl-substituted toluene derivative which comprises heating about 200 parts by weight of toluene and less than 200 parts by weight of ethylene with about 0.2 part of benzalazine at a temperature of about 200° to 300° C. under a pressure in the range of 400 to 1500 atmospheres, whereby a waxy alkyl-substituted toluene is formed, and thereafter separating the said waxy product from the resultant mixture.

17. A waxy product consisting essentially of a mixture of compounds of the formula $H(CH_2CH_2)_nR$, in which R is a monovalent hydrocarbon radical derived from a short-chain alkyl benzene by removal of a single hydrogen atom, n being an integer from 7 to 50, said waxy product having been prepared by reacting a short chain alkyl-substituted aromatic hydrocarbon with ethylene in the presence of a catalyst containing the >C=N— grouping, said catalyst being selected from the class consisting of oximes, hydrazones, azines, semicarbazones, Schiff's bases and anils of ketaldones, at a temperature in the range of about 200° to 300° C., under a pressure in the range of 400 to 1500 atmospheres.

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Certificate of Correction

Patent No. 2,432,381. December 9, 1947.

DONALD D. COFFMAN ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Column 1, line 40, for "$H(HC_2CH_2)_nR$" read $H(CH_2CH_2)_nR$; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of February, A. D. 1948.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.