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CHLORINATION OF NORMAL PARAFFINS IN THE PRESENCE OF BENZENE AND ALKYLATION OF THE BENZENE

Daniel J. Hurley, Oakmont, Robert W. Rosenthal, Pittsburgh, and Roger C. Williamson, Gibsonia, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

No Drawing. Continuation-in-part of application Ser. No. 329,232, Dec. 9, 1963. This application July 16, 1964, Ser. No. 383,234

5 Claims. (Cl. 260—671)

This application is a continuation-in-part of our application, Ser. No. 329,232, filed Dec. 9, 1963, and now abandoned.

This invention relates to a process for chlorinating a normal paraffin or a mixture of normal paraffins, the composition resulting therefrom and a process for alkylating an aromatic, such as benzene, with said composition.

When a normal paraffin having, for example, from six to 20 carbon atoms in the molecule, is subjected to chlorination by passing chlorine therethrough in the presence of a light source, such as actinic light, primary and secondary normal alkyl chlorides are formed. Benzene, for example, can be alkylated in the presence of an alkylation catalyst, such as aluminum chloride, with the normal alkyl chlorides so produced. We have found, however, that while benzene can be alkylated with the secondary normal alkyl chlorides rather easily, alkylation with the primary normal alkyl chlorides is relatively more difficult. In order to alkylate benzene with both secondary and primary normal alkyl chlorides, a relatively long alkylation period is required, or, if a shorter alkylation period is desired, a much higher concentration of alkylation catalyst must be employed.

We have now found that the amount of primary normal alkyl chlorides produced can be substantially reduced and the amount of secondary normal alkyl chlorides correspondingly increased when a normal paraffin having from six to 20 carbon atoms, or mixtures thereof, are subjected to chlorination by passing chlorine therethrough in the presence of a light source, such as actinic light, while said normal paraffin is dissolved in benzene. As a result thereof, when an aromatic, such as benzene, is subjected to alkylation with the alkyl chlorides so produced, less time is required to alkylate the aromatic with all of the alkyl chlorides or less catalyst can be employed than would be the case if the aromatic were to be alkylated with normal alkyl chlorides similarly produced but in the absence of benzene. An additional advantage resulting from the chlorination of the normal paraffin in benzene, in the case wherein the normal alkyl chlorides are to be used to alkylate benzene, resides in the fact that upon completion of the chlorination, the alkylation catalyst can be added to the mixture and alkylation of the benzene with the normal alkyl chlorides can then proceed. Of course, if desired, the normal alkyl chlorides so obtained can be separated from the benzene by simple fractionation, since the boiling point of benzene and the normal alkyl chlorides are far apart, and the normal alkyl chlorides so recovered can be used to alkylate fresh benzene or any other aromatic or used in any desired manner.

A particularly attractive embodiment of our invention resides in the alkylation of benzene with a mixture of primary and secondary normal alkyl mono-chlorides, wherein the alkyl portion thereof has from 10 to 16 carbon atoms, particularly from 11 to 14 carbon atoms, to produce an alkyl benzene mixture, commonly referred to as "detergent alkylate," since it can be subsequently sulfonated in the known manner to produce a detergent.

The normal paraffin, or mixtures of normal paraffins,

that are chlorinated in accordance with the procedure defined herein to form the new composition of matter can have from six to 20 carbon atoms. Such normal paraffins include hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane and eicosane. In accordance with the preferred embodiment of this invention, wherein a detergent alkylate is produced from the normal alkyl chlorides, a mixture containing C_{10}, C_{11}, C_{12}, C_{13}, C_{14}, C_{15} and C_{16} normal paraffins, particularly C_{11}, C_{12}, C_{13}, and C_{14} normal paraffins, is subjected to the defined chlorination procedure. The latter mixture can be obtained in any suitable manner, but preferably is obtained by treating a kerosene in the known manner with urea to form an adduct of urea and normal paraffins having from 10 to 16 carbon atoms. The adduct is thereafter decomposed and the desired mixture of C_{10} to C_{16} normal paraffins is thereby obtained. Alternatively, these mixtures can also be obtained by treating a kerosene in known manner, using molecular sieves to separate the C_{10} to C_{16} normal paraffins therefrom.

The chlorination procedure of this invention is effected while the defined normal paraffin or mixtures of the defined normal paraffins are dissolved in benzene. The chlorination can then be carried out in any suitable manner, but desirably is performed merely by passing gaseous chlorine through the mixture of normal paraffin or normal paraffins and benzene in the presence of a suitable light source, such as actinic light. Such light can be defined as one having a wave length of from about 2000 to 6000 A., preferably from about 3500 to 4500 A. The temperature during the chlorination can be from about 10° to about 78° C., preferably about 15° to about 28° C. The lower temperatures are desired, however, since at lower temperatures there will be tendency to form less of the primary normal alkyl chlorides. The amount of primary normal alkyl chlorides formed at any temperature level, however, within the defined temperature ranges, will be less when the chlorination is effected in accordance with the dictates of this invention in benzene than without. Pressures can be from about atmospheric to about 10 pounds per square inch gauge. Increased pressure increases the rate of chlorination, but adversely affects the course of the reaction by increasing the percent of primary alkyl chloride produced.

The amount of gaseous chlorine passed through the mixture is not critical, except as the amount thereof is increased the amount of chlorination resulting therefrom is also increased. In general, good results will be obtained by passing through the mixture about 0.1 to about 0.3 mol of chlorine per mol of normal paraffins in the desired reaction time. Reaction time is not critical as long as the addition allows time for good mixing and heat dissipation. The amount of benzene present affects the amounts of primary normal alkyl chlorides obtained. Increasing the amount of benzene in the mixture being subjected to the action of chlorine results in the formation of lesser amounts of primary normal alkyl chlorides. In general about two to about 20 mols of benzene, preferably about two to about seven mols of benzene, per total mol of normal paraffins is satisfactory.

The extent of chlorination of the normal paraffins is not critical and any amount thereof can be chlorinated, even to the replacement of each hydrogen thereon with a chlorine atom. However, in the preferred embodiment wherein a detergent alkylate is produced using the alkyl chlorides obtained herein, chlorination as defined herein is continued until up to about 30 molecules of chlorine, preferably from about 20 to about 30 molecules of chlorine, but most desirably about 25 molecules of chlorine, are reacted with every 100 molecules of normal paraffins present. Up to this point almost all of the alkyl chlorides

obtained are primary and secondary normal alkyl monochlorides. Further chlorination, however, results in increased amounts of normal alkyl polychlorides. When the chlorinated mixture is thereafter employed in the alkylation of benzene alkylation will also result between the normal alkyl polychlorides and the benzene to form indanes and generally undesirable diphenyl alkanes.

The desired alkylation when the aromatic to be alkylated is benzene, can then be carried out merely by introducing the alkylation catalyst into the chlorinated mixture. Suitable alkylation catalysts include Lewis type alkylation catalysts such as $AlCl_3$, $SnCl_4$, $SbCl_5$, $TiCl_4$, BCl_3, $ZnCl_2$, $HgCl_2$, HF, etc. Aluminum chloride is preferred. The amount of catalyst employed, relative to the alkyl monochlorides present, is about three to about 10 percent by weight. The alkylation mixture can contain from about five to about 15 mols of the aromatic, preferably from about six to about eight mols of the aromatic, per total mol of normal alkyl chlorides. Depending upon the amount of benzene that was present in admixture with the normal paraffins during the chlorination procedure, additional benzene will be added thereto or excess benzene removed therefrom. Since the boiling point of the benzene and boiling points of the remaining components in the chlorination mixture are widely separated, simple fractionation at a temperature of 75° to about 85° C. at atmospheric pressure will suffice for removal of benzene therefrom. In the event, however, that a detergent alkylate is to be produced, and therefore only a selected portion of the normal paraffins have been chlorinated, the alkylation of benzene with the normal alkyl chlorides is effected in the presence of the unreacted normal paraffins. Separation of alkyl chlorides from unreacted normal paraffins can not, normally, be easily carried out, since high temperatures are required and at such high temperatures the alkyl chlorides tend to dehydrochlorinate to internal olefins. Of course, in the event the normal alkyl chlorides are not to be used to alkylate benzene, they are separated therefrom in the manner described above. Other aromatics, for example toluene, naphthalene, thiophene, xylene, etc., can be alkylated with the normal alkyl chlorides if desired.

The alkylation is carried out in the normal manner. Temperatures on the order of about 15° to about 70° C. and pressures of about 250 mm. of mercury to about 100 pounds per square inch gauge are satisfactory. A reaction period of about one-half to about one and one-half hours will suffice. During the reaction gaseous hydrogen chloride will be given off and can be permitted to escape from the reaction zone. Upon completion of the reaction, the catalyst will settle as a sludge to the bottom of the reaction vessel and the reaction mixture can thus be separated therefrom. The reaction mixture can then be washed with about five to about 50 percent solution of a base, such as sodium hydroxide, potassium hydroxide, calcium hydroxide, barium hydroxide, etc., to remove residual hydrogen chloride therefrom and thereafter with about 10 to about 25 percent by volume of water to remove base and any hydrogen chloride still present. The resulting mixture is then fractionated at atmospheric pressure and a temperature of about 70° to about 85° C. to remove benzene or other aromatic therefrom. Thereafter at a reduced pressure of about one to about 20 mm. Hg and a temperature of about 100° to about 200° C. unreacted paraffin and the desired alkyl benzene are successively removed. Heavier products remain behind.

We have found that the chlorination procedure defined herein not only results in a composition having a lower primary alkyl monochloride content but also an unusual and unexpected distribution of secondary alkyl monochloride isomers as "internal" secondary alkyl monochlorides and "external" secondary alkyl monochlorides. By "internal" secondary alkyl monochlorides we mean to include only those secondary alkyl monochlorides wherein the chlorine in the molecule is at least two carbon atoms away from the terminal carbon atom. By "external" secondary alkyl monochlorides we mean to include only those secondary alkyl monochlorides wherein the chlorine in the molecule is adjacent to or one carbon removed from the terminal carbon atom. When a normal paraffin is chlorinated in the manner defined herein, but in the absence of benzene, the primary alkyl monochloride content is higher, as noted, but the external secondary alkyl monochloride content remains substantially constant while the internal secondary alkyl monochloride content is lower. The isomer distribution obtained when a normal paraffin is chlorinated in benzene in accordance with the procedure defined herein is especially desirable when a C_{10} to C_{16}, particularly a C_{11} to C_{14}, alkyl monochloride produced herein is employed to produce a detergent alkylate.

The isomer distribution of the normal alkyl monochlorides obtained when a normal paraffin, or a mixture of normal paraffins, having from 11 to 14 carbon atoms is chlorinated in benzene in accordance with the procedure defined herein can be defined by reference to the following:

TABLE I

	Monochloride Isomer Distribution, Weight percent		
	1-isomer	2 and 3-isomers	Remaining isomers
Normal Alkyl Monochloride:			
C_{14}	1–9	30–36	59–65
C_{13}	1–9	23–38	57–63
C_{12}	1–9	35–41	55–61
C_{11}	1–9	40–44	51–57

The isomer distribution obtained when the normal paraffins are chlorinated in accordance with the procedure defined herein, but in the absence of benzene, can be defined approximately by reference to the following:

TABLE II

	Monochloride Isomer Distribution, Weight percent		
	1-isomer	2 and 3-isomers	Remaining isomers
Normal Alkyl Monochloride:			
C_{14}	7–10	23–34	56–58
C_{13}	8–12	34–36	53–55
C_{12}	10–14	37–39	51–53
C_{11}	11–15	42–44	45–47

A comparison of the data in Table I with Table II shows that when a normal paraffin, or mixture of normal paraffins, is chlorinated in benzene in accordance with the procedure defined herein there is a change in isomer distribution from the 1-chloro isomer to the internal isomers. This is unusual since it would have been expected that the loss in primary isomer content would be equally distributed among the secondary carbon atoms on the molecule. As noted these alkyl chlorides are desirably employed to alkylate benzene to form detergent alkylates, which are then converted in known manner to form alkyl benzene sulfonate detergents. In general when benzene is alkylated with the normal alkyl chlorides produced herein to form a detergent alkylate, the overall result is that the chlorine atom is replaced by the benzene with the formation of hydrogen chloride. It is known that an alkyl benzene sulfonate wherein the benzene portion thereof is attached to the alkyl portion on an "internal" carbon thereof is a detergent having increased foam stability without a sacrifice in detergency. Accordingly since the detergent alkylate produced herein has a high internal isomer content, it is obvious that the detergent alkylate produced herein is an extremely desirable product for its intended purpose. However, in order to maintain approximately the same isomer distribution in the detergent alkylate that

was present in the normal alkyl monochlorides obtained, it is imperative that the alkylation of the benzene with the normal alkyl monochlorides be effected under the conditions defined herein in the presence of about two to about eight percent by weight, preferably about five percent by weight, of aluminum chloride based on the alkyl monochlorides present. When the amount of aluminum chloride employed is above the defined amounts, the desired isomer distribution is no longer maintained and carried over to the detergent alkylate.

The process of this invention can further be understood by reference to the following.

EXAMPLE I

In one experiment there was placed in a one liter container 368 grams of normal dodecane and in another similar container there were placed 200 grams of dodecane and 352 grams of benzene. In each case, while the contents of the container were stirred there was passed therethrough over a period of 40 minutes gaseous chlorine at a rate of one gram per minute. During the chlorination procedures the light from a 150 watt G.E. bulb was maintained on the reaction mixture, and the temperature was maintained at 75° C. and the pressure at 0 pound per square inch gauge. Aluminum chloride was then added to the chlorinated mixture and alkylation was effected at a temperature of 28° C. and a pressure of 0 pound per square inch gauge. The results obtained are tabulated below in Table III.

TABLE III

Experiment Number	Benzene	Chlorination: Mol Percent Dodecane Chlorinated	Chlorination: Mol Percent Primary Normal Alkyl Chloride Based On Total Alkyl Monochloride	Alkylation: Molar Ratio Of Benzene To Total Normal Alkyl Monochloride	Alkylation: Weight Percent $AlCl_3$ Based On Total Alkyl Monochloride	Alkylation: Time, Minutes	Alkylation: Percent Of Total Alkyl Monochloride Reacted
1	None	31	11.6	19.2	4.98	15	92.2
						30	94.3
						45	95.9
						60	97.1
						75	97.3
						90	98.8
						105	99.3
2	Four mols per mol of Dodecane	30	6.8	19.2	4.97	15	97.8
						30	99.7
						45	100

The above data clearly show that when a normal paraffin is chlorinated in benzene, and therefore the amount of primary normal alkyl chloride is reduced, the subsequent alkylation of benzene with the alkyl chlorides so produced is accelerated. Thus in Experiment No. 2 the alkylation of benzene with the alkyl chlorides was complete in 45 minutes, whereas the alkylation of benzene with the alkyl chlorides produced in the absence of benzene was only 95.9 percent complete at the end of 45 minutes. In fact, in Experiment No. 1 the alkylation was not complete even at the end of 105 minutes.

That the amount of primary normal alkyl chloride formed is progressively reduced as the amount of benzene in the mixture being chlorinated is increased is seen from the following.

EXAMPLE II

Dodecane alone and in admixture with benzene was placed in a container, and at a temperature of 75° C. and a pressure of 0 pound per square inch gauge chlorine at the rate of 0.5 to two grams per minute was passed therethrough over a period of 30 minutes until a 0.25 gram atom of chlorine had reacted for each mol of dodecane present. The results obtained are tabulated below in Table IV.

TABLE IV

Mols of benzene per mol of dodecane	Percent by weight of primary normal alkyl monochloride based on total normal alkyl monochlorides
0	13.4
3.7	8.5
6.1	7.6
20.0	6.8

That similar results will occur at lower temperatures with the formation of even lesser amounts of primary normal alkyl monochlorides is seen from the following.

EXAMPLE III

The operation of Example II was repeated, except that the chlorination was conducted at a temperature of 35° C. The results are tabulated below in Table V.

TABLE V

Mols of benzene per mol of dodecane	Percent by weight of primary normal alkyl monochloride based on total normal alkyl monochlorides
0	11.5
3	6.2

EXAMPLE IV

To determine whether or not the same results obtained above would be obtained if a mixture of normal paraffins were to be chlorinated in benzene a mixture containing 0.125 mol of undecane, 0.125 mol of dodecane and 0.75 mol of benzene was subjected to chlorination under the conditions of Example II. The molar ratio of benzene in this situation relative to the dodecane was therefore 6:1. The percent of primary normal C_{12} monochloride relative to all of the C_{12} monochlorides obtained was 7.5 percent. This compares well with the comparable run in Example II. Determination of the amount of normal C_{11} monochlorides obtained was not made because the retention time, under the gas-liquid chromatography test employed for analysis, of the dodecane was the same as the retention time of the normal C_{11} monochlorides.

EXAMPLE V

The chlorination procedure of Example II was repeated with a mixture of benzene and tetradecane in a molar ratio of 20:1. The amount of primary normal C_{14} monochloride obtained amounted to 6.9 percent based on the total C_{14} monochlorides produced.

EXAMPLE VI

A series of chlorination runs was made in accordance with the procedure and conditions defined in Example I. In each run one mol of a defined paraffin was chlorinated both in the presence of benzene and in the absence of benzene. The resulting solutions were analyzed by gas-liquid chromatography. The results are tabulated below in Table VI.

TABLE VI

Normal Paraffin Chlorinated	Mol Ratio of Benzene To Normal Paraffin During Chlorination	Monochloride Isomer Distribution, Weight Percent		
		1-isomer	2 and 3-isomers	Remaining isomers
C_{13}	0	10.5	35.6	53.9
C_{13}	5	5.1	35.1	59.8
C_{12}	0	9.8	38.3	51.9
C_{12}	4	3.5	37.9	58.6
C_{11}	0	11.0	43.0	46.0
C_{11}	4	4.3	42.0	53.7

The above data clearly show that chlorination of a normal paraffin in benzene reduces the primary monochloride content and increases the internal secondary alkyl monochloride content while leaving the external secondary alkyl monochloride content relatively unchanged.

EXAMPLE VII

A series of alkylation runs was made in accordance with the procedure and conditions defined in Example I using alkyl monochloride solutions obtained in Example VI and benzene wherein the total benzene relative to the alkyl monochlorides was maintained in a molar ratio of about 20:1 and the aluminum chloride was maintained at about five percent by weight based on the alkyl monochlorides present. The results, obtained by mass spectrometric analysis, are tabulated below in Table VII.

TABLE VII

Normal Paraffin Chlorinated	Mol Ratio of Benzene To Normal Paraffin During Chlorination	Phenyl Isomer Distribution In Detergent Alkylate, Weight Percent						
		1-Ph	2-Ph	3-Ph	4-Ph	5-Ph	6-Ph	7-Ph
C_{13}	0	0.8	26.5	20.5	14.9	16.2	14.1	6.9
C_{13}	5	0.7	25.7	20.3	15.3	16.4	14.6	7.1
C_{12}	0	0.8	30.6	21.5	16.1	16.2	14.5	-------
C_{12}	4	0.8	28.1	21.8	16.6	16.8	15.8	-------
C_{11}	0	1.6	34.9	22.3	15.4	17.3	8.6	-------
C_{11}	4	0.6	33.9	21.9	16.0	18.3	9.3	-------

The above data clearly show that the alkyl chloride obtained when the normal paraffins were chlorinated in benzene when subsequently reacted with benzene in the presence of five percent by weight of aluminum chloride resulted in a detergent alkylate having a decrease in the 2-phenyl isomer content and an increase in the 5- and 6-phenyl isomers.

EXAMPLE VIII

The two chlorinated C_{13} solutions formed in Example VI were then alkylated with 10 percent aluminum chloride in accordance with the procedure described in Example VII. The results, obtained by mass spectrometric analysis, are tabulated below in Table VIII.

TABLE VIII

Mol Ratio of Benzene To Normal Paraffin During Chlorination	Phenyl Isomer Distribution In Detergent Alkylate, Weight Percent						
	1-Ph	2-Ph	3-Ph	4-Ph	5-Ph	6-Ph	7-Ph
0	0.8	28.4	19.7	15.3	15.2	13.9	6.6
5	0.8	28.3	19.7	15.0	15.6	13.7	7.0

The above data show that when the amount of aluminum chloride employed was raised to 10 percent by weight the phenyl isomer distribution in the detergent alkylate was substantially the same whether or not the normal alkyl monochlorides employed during the alkylation were obtained by chlorinating the normal paraffin in benzene or in the absence of benzene.

The alkyl benzenes wherein the alkyl portion thereof has from 11 to 14 carbon atoms produced using the mixture of C_{11} to C_{14} normal alkyl chlorides obtained herein are, as stated, commonly referred to as "detergent alkylates," since they can be reacted with a sulfonating agent, such as sulfuric acid, oleum or sulfur trioxide, and then neutralized to form alkyl benzene sulfonate detergents. The remaining alkyl aromatics obtained using the remaining normal alkyl chlorides obtained herein can be employed as wetting agents or oil-soluble detergents.

Obviously many modifications and variations of the invention, as hereinabove set forth, can be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process which comprises passing gaseous chlorine through a mixture containing benzene and at least one normal paraffin selected from the group consisting of normal paraffins having from 10 to 16 carbon atoms, two to 20 mols of benzene being used per mol of normal paraffin, in the presence of light, at a temperature of 10° to 78° C. and thereafter alkylating the same benzene with the normal alkyl chlorides so produced in the presence of an alkylation catalyst.

2. A process which comprises passing gaseous chlorine through a mixture containing benzene and at least one normal paraffin selected from the group consisting of normal paraffins having from 10 to 16 carbon atoms, two to 20 mols of benzene being used per mol of normal paraffin, in the presence of light, at a temperature of 10° to 78° C., and thereafter alkylating the same benzene with the normal alkyl chlorides so produced in the presence of about two to about eight percent by weight of aluminum chloride.

3. A process which comprises passing gaseous chlorine through a mixture containing benzene and at least one normal paraffin selected from the group consisting of normal paraffins having from 10 to 16 carbon atoms, two to 20 mols of benzene being used per mol of normal paraffin, in the presence of light, at a temperature of 10° to 78° C., and thereafter alkylating the same benzene with the normal alkyl chlorides so produced in the presence of about five percent by weight of aluminum chloride.

4. A process which comprises passing gaseous chlorine through a mixture of benzene and C_{10} to C_{16} normal paraffins, wherein the molar ratio thereof is about two to about 20, at a temperature of about 10° to about 78° C., in the presence of light, resulting in a second mixture containing benzene, unreacted normal paraffins and predominantly C_{10} to C_{16} primary and secondary normal monochlorides and thereafter alkylating the same benzene with said primary and secondary normal monochlorides in the presence of aluminum chloride.

5. A process which comprises passing gaseous chlorine through a mixture of benzene and C_{10} to C_{16} normal paraffins, wherein the molar ratio thereof is about two to about 20, at a temperature of about 10° to about 78° C., in the presence of light, resulting in a second mixture containing benzene, unreacted normal paraffins and predominantly C_{10} to C_{16} primary and secondary normal monochlorides and thereafter alkylating benzene with said primary and secondary normal monochlorides in the presence of aluminum chloride, the benzene that is alkylated being the same benzene in the mixture being chlorinated.

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LEOW ZITVER, *Primary Examiner.*

T. G. DILLAHUNTY, *Assistant Examiner.*

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,418,388 December 24, 19

Daniel J. Hurley et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, TABLE I, third column, line 2 thereof, "23-38" should read -- 32-38 --; same column, TABLE II, third column, line 1 thereof, "23-34" should read -- 32-34 --.

Signed and sealed this 17th day of March 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents