Patented Oct. 14, 1952

2,614,130

UNITED STATES PATENT OFFICE

2,614,130

OXIDATIVE CONDENSATION OF ALKYL AROMATIC HYDROCARBONS AND OF NUCLEARLY CHLORINATED ALKYL AROMATIC HYDROCARBONS

Herman Pines, Bruno Kvetinskas, and Vladimir N. Ipatieff, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

No Drawing. Application March 26, 1949, Serial No. 83,774

9 Claims. (Cl. 260—649)

1

This invention relates to a process for oxidizing alkyl aromatic compounds and particularly for oxidizing a member of the group consisting of alkyl aromatic hydrocarbons and nuclearly chlorinated alkyl aromatic hydrocarbons to effect the formation of a diarylalkane or of a nuclearly chlorinated diarylalkane.

An object of this invention is to produce a diarylalkane hydrocarbon.

Another object of this invention is to produce a nuclearly chlorinated diarylalkane.

One specific embodiment of this invention relates to a process for producing a member of the group consisting of a diarylalkane and a nuclearly chlorinated diarylalkane which comprises reacting in the presence of at least one member of the group consisting of magnesium and aluminum, a gas containing free oxygen and a member of the group consisting of an aromatic hydrocarbon and a nuclearly chlorinated aromatic hydrocarbon each having an alkyl group containing at least one and not more than two hydrogen atoms combined with the carbon atom attached to the aromatic ring.

Another embodiment of this invention relates to a process for producing a diphenylalkane which comprises reacting in the presence of aluminum a gas containing free oxygen and a benzene hydrocarbon having an alkyl group of at least two carbon atoms and containing at least one hydrogen atom combined with the carbon atom attached to the benzene ring.

A further embodiment of this invention relates to a process for producing a nuclearly chlorinated diphenylalkane which comprises reacting in the presence of aluminum a gas containing free oxygen and a nuclearly chlorinated alkyl benzene hydrocarbon in which said alkyl group contains at least two carbon atoms and at least one hydrogen atom combined with the carbon atom attached to the benzene ring.

We have found that the treatment in the presence of at least one metal of the group consisting of magnesium and aluminum of certain alkyl aromatic hydrocarbons and nuclearly chlorinated alkyl aromatic hydrocarbons with air, oxygen, or oxygen in admixture with an inert gas or mixture of inert gases results in the removal of hydrogen from said alkyl aromatic compounds and the production of an aromatic hydrocarbon of higher molecular weight including a diarylalkane and a di(chloroaryl) alkane.

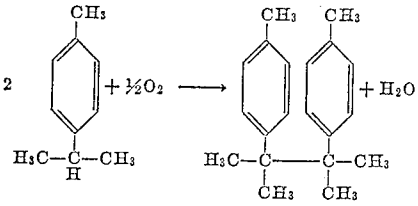
2

The aromatic compounds suitable for use in this process include alkyl aromatic hydrocarbons and nuclearly chlorinated alkyl aromatic hydrocarbons each containing an alkyl group of at least two carbon atoms and containing at least one hydrogen atom combined with the carbon atom of said alkyl group attached to the aromatic ring. While the aromatic ring of said starting material is preferably a benzene ring, it may also be a polycyclic ring including at least one benzene ring such as a naphthalene ring, a tetralin ring, or other polycyclic aromatic hydrocarbon ring. Accordingly, aromatic hydrocarbons which may be so used as starting materials in our process include ethylbenzene, cumene, cymene, propylbenzene, butylbenzene, sec.-butylbenzene, isobutylbenzene, and higher boiling monoalkyl, dialkyl, and other polyalkyl benzenes in which the carbon atom of an alkyl group attached to the benzene ring is also attached to one but not more than two hydrogen atoms. Nuclearly chlorinated alkyl aromatic hydrocarbons having an alkyl group containing at least one and not more than two hydrogen atoms bound to the carbon atom attached to the aromatic ring are also suitable starting materials for producing a di(chloroaryl) alkane.

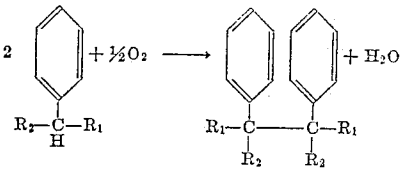
We have found that the above indicated alkyl aromatic hydrocarbons and nuclearly chlorinated alkyl aromatic hydrocarbons may be reacted with air, oxygen, or a mixture of an inert gas and oxygen at a temperature of from about 100° to about 250° C. and preferably at a temperature of from about 125° to about 200° C. with the hydrocarbon material preferably in liquid phase. In order to maintain the hydrocarbons in liquid phase, it may be necessary to use superatmospheric pressure, but generally not in excess of about 100 atmospheres. The gaseous oxidizing agent such as air or a mixture of inert gases and oxygen are then contacted with the liquid aromatic compound in order to effect condensation to form diarylalkanes and nuclearly chlorinated diarylalkanes.

As an illustration of this process, we found that by reacting paracymene with air at controlled conditions of temperature within the above indicated range, a reaction occurred whereby two

molecular proportions of paracymene condensed with or reacted with each other to form 2,3-dimethyl-2,3-ditolyl butane and water as illustrated by the following equation:



The above indicated reaction may also be applied to other alkyl aromatic hydrocarbons such as dialkyl aromatic hydrocarbons. Such a reaction is illustrated by the following equation in which R_1 and R_2 represent alkyl groups each separately and independently containing at least two carbon atoms and generally containing from about 2 to about 4 carbon atoms and said aromatic hydrocarbons containing less than four of said R groups per molecule:



This oxidative condensation of an aromatic hydrocarbon such as paracymene is accompanied by the formation of oxygenated compounds such as carbinols, ketones, and higher boiling products in addition to the diarylalkane formed as indicated in the foregoing equations.

Similarly, the oxidation treatment of parachloroisopropylbenzene (sometimes referred to as parachlorocymene) is carried out in the presence of aluminum turnings or magnesium turnings which serve as condensation catalyst. In the presence of the aluminum turnings a yield of 7% per pass is obtained of the condensation product herein referred to as 2,3-dimethyl-2,3-p-chlorophenylbutane.

This process may be carried out in either batch or continuous types of operation. In a typical batch-type operation, the aromatic hydrocarbon, metallic aluminum (generally in the form of turnings) sometimes also a base such as sodium carbonate, potassium carbonate, etc., are placed in a reactor heated to a temperature of from about 100° to about 250° C. and maintained at a pressure sufficient to keep a substantial proportion of the hydrocarbons and chlorinated aromatic hydrocarbons in liquid phase while air or another gas containing free oxygen is passed therethrough. The use of a basic material and also at least one metal selected from the members of the group consisting of magnesium and aluminum promotes the formation of a high yield of diarylalkane or nuclearly chlorinated diarylalkane depending upon the type of the charging stock charged to the process.

In continuous operation, an alkyl aromatic hydrocarbon or nuclearly chlorinated alkyl aromatic hydrocarbon of the type indicated herein and air or oxygen or some other oxygen containing gas are passed through a heated reactor containing at least one of the metals selected from the members of the group consisting of magnesium and aluminum and having atomic numbers 12 and 13 and the resultant reaction products are then recovered and separated into the condensation products and unconverted starting materials, the latter being suitable for further treatment in the process.

The following examples are given to illustrate the type of results obtained in this process although the data presented are not introduced with the intention of restricting unduly the broad scope of the invention.

EXAMPLE I

Batch-type runs were made by placing an aromatic hydrocarbon in a flask and heating therein to the desired temperature while air was bubbled into the hydrocarbon through a flow meter. At the end of the run the current of air was shut off, the peroxide number of the product was determined and the product was distilled without further treatment for in no case was the peroxide number dangerouly high. The unreacted hydrocarbon was distilled off at atmospheric pressure, the remaining product was cooled and filtered with suction to remove crystalline products and the liquid filtrate was fractionally distilled at reduced pressure. Some of the fractions were examined by infra-red absorption methods to determine the amount of ketone, alcohol, and diaryl alkanes present. Thus on heating p-cymene at 173° C. and passing air through the heated hydrocarbon at a rate of 2.8 liters per hour for 20 hours, a total of 32 grams of higher boiling product was obtained containing 50% of p-methylacetophenone, 27% of 2,3-dimethyl-2,3-ditolylbutane, which may also be called dicymene, and 23% of an intermediate fraction containing some dicymene.

EXAMPLE II

In order to increase the yield of dicymene, other oxidation runs were made by treating p-cymene with air in the presence of metallic aluminum. The aluminum contacting material in an amount of about 400 cc. was placed in the reaction flask into which was introduced 600 grams of cymene. The latter was heated to a reflux temperature under a reflux condenser and a stream of air was passed through the heated hydrocarbon at a rate of 12 liters per hour. It was found that the presence of the aluminum packing material increased the yield of oxidation products obtained from p-cymene.

In another run the oxidation treatment of p-cymene was carried out for a time of 18 hours in the presence of aluminum turnings and potassium carbonate. The results obtained in these two runs, that is, in the presence of aluminum turnings, and in a mixture of aluminum turnings and potassium carbonate are summarized by the following table:

Table I

Experiment No.	1	2
p-Cymene, g.	600	600
Aluminum turnings, grams	200	214
Potassium Carbonate, grams	None	20
Air rate, liters/hr.	12	12
Temperature, ° C.	171	172
Time on stream, hrs.	18	18
Results:		
Reacted product, weight percent	13	17
Composition of reacted products, percent—		
Ketones and Carbinols	28	35
Dairylalkanes [1]	27	33
Bottoms	27	7

[1] Composition: 2,3-dimethyl-2,3-di(p-tolyl)butane.

From the above indicated results, it is evident that the production of dicymene was greater in the presence of both aluminum turnings and potassium carbonate than in the

presence of aluminum turnings alone. That is, the yield of di-p-cymene was increased from 27 to 33% and the yield of ketone-carbinol fraction was also increased from 28 to 35% while the amount of higher boiling products (indicated in the table as bottoms) was reduced from 45 to 29%.

EXAMPLE III

By following essentially the same procedure as that in Example II, 12 liters of air per hour were passed through 600 grams of p-cymene maintained at a temperature of 172° C. during a time of 18 hours. The p-cymene being treated was in contact with 165 grams (400 cc.) of magnesium turnings and also 20 grams of potassium carbonate. At the end of this treatment, the liquid oxidation product had a peroxide number of 17.3, a refractive index n_D^{20} of 1.4968. During this treatment there were formed 5.4 cc. of water and 76.3 grams of reaction product boiling higher than p-cymene. The reaction product so obtained boiling higher than p-cymene contained 4.2% of organic acids, 39% of a mixture of p-methyl-p-tolyl carbinol, 16.1% of higher boiling liquids, 28% of 2,3-dimethyl-2,3-di-p-tolylbutane, and 12.7% of residue.

EXAMPLE IV

Following the procedures of Examples II and III, 600 grams of cumene was heated to a temperature of 148–149° and treated by bubbling air therethrough for 18 hours at a rate of 12 liters per hour. In one of these runs, 400 cc. of aluminum turnings were present in the reactor containing the cumene while in the other run soft glass rings were used. The results obtained in these two runs are summarized by the following table:

Table II

Experiment No.	6	8
Aromatic charged:		
Kind	Cumene	Cumene
grams	600	600
Contact medium:		
Kind	Soft glass rings.	Al turnings,
cc.	400	400
Additive:		
kind		
grams		
Air rate, liters/hr.	12	12
Temperature, ° C.	148	148
Time on stream, hr.	18	18
Results:		
Peroxide No.	303	6.4
n_D^{30} of product	1.4964	1.4967
Total water formed, cc.	2.5	4.6
Reacted product:		
grams	60.1	56.1
weight percent [1]	10.4	10.2
Composition of unreacted product (excluding unreacted charged):		
Acid	0.3	0.0
Keton+Carbinol [2]	82.6	60.9
Higher boiling liquid	4.8	7.3
Diarylalkane [3]	9.1	26.9
Bottoms	3.2	4.9
Analysis of Ketone-carbinol fraction, percent:		
Ketone	42	57
Carbinol	58	43

[1] The weight of product taken for distillation after washing and drying is used for this calculation.
[2] When cumene is charged it is acetophenone+dimethylphenyl carbinol.
[3] When cumene is charged it is 2,3-dimethyl-2,3-diphenylbutane.

In the presence of the soft glass rings, the reaction product contained 10.4% by weight of reacted material which consisted of 82.6% of a ketone-carbinol fraction, 9.1% of dicumene and 8.0% of higher boiling material. The presence of aluminum turnings in the reaction zone markedly increased the yield of the dicumene and decreased the yield of the ketone-carbinol fraction. The amount of reacted material in the product was 10.2%. The reaction products boiling higher than cumene consisted of 60.9% of ketone-carbinol fraction, 26.9% of dicumene and 12.2% higher boiling liquid and bottoms when aluminum turnings were present in the reaction zone.

When the metals magnesium and aluminum were used as contacting media in the oxidation of cumene and p-cymene, the yield of diarylalkane and high boiling products was increased over that obtained in the absence of the metal while the ketone-carbinol yield was increased. The addition of potassium carbonate to the metal resulted in the formation of a cleaner oxidation product which contained smaller amounts of high boiling residue but larger amounts of ketone-carbinol fraction and also larger amounts of diarylalkanes.

EXAMPLE V

s-Butylbenzene was reacted with air for 18 hours at 169° in the presence of aluminum turnings and potassium carbonate. The product contained 12.9 weight per cent of material boiling higher than the charge, of this, 0.7% was acid, 53% boiled in the ketone-carbinol range, 17.3% was a crystalline dimer of s-butylbenzene, 21.4% high boiling liquid, and 7.6% remained as bottoms. The structure of the crystalline dimer is that of 3,4-dimethyl-3,4-diphenylhexane. Recrystallized from 95% ethanol it melted at 97–98°.

EXAMPLE VI

p-Chlorocumene was reacted for 18 hours with air at 171° in the presence of potassium carbinate using aluminum turnings as a contact material in one case and glass rings in another case. The weight per cent of product boiling higher than the charge was 15.4 when aluminum turnings were employed and 26.8 when glass rings were used. On recycle basis, when aluminum turnings were used, the product consisted of 1.9% acids, 70.8% ketone-carbinol fraction, 12.7% higher boiling liquid, 6.9% di-p-chlorocumene, and 7.7% resinous bottoms; and when glass rings were used, it consisted of 2.4% acids, 85.7% ketone-carbinol fraction, 5.4% higher boiling liquid, 1.2% di-p-chlorocumene and 5.3% resinous bottoms. The yield of dimer from p-chlorocumene was not nearly as high as that obtained from p-cymene or cumene but the effect of the aluminum is in the same direction, that is, it increased the yield of dimer. The structure of the crystalline di-p-chlorocumene is indicated as 2,3-di-p-chlorophenyl-2,3-dimethylbutane. Recrystallized from absolute ethanol, it melted at 166–167°.

We claim as our invention:

1. A process for producing a member of the group consisting of a diarylalkane and a nuclearly chlorinated diarylalkane from an aromatic compound of the group consisting of an aromatic hydrocarbon and a nuclearly chlorinated aromatic hydrocarbon each having an alkyl group containing at least one and not more than two hydrogen atoms combined with the carbon atom attached to the aromatic ring, which comprises subjecting said aromatic compound to oxidative condensation by reacting the same with free oxygen at a temperature of from about 100° to about 250° C. in the presence of at least one metal of the group consisting of aluminum and magnesium.

2. A process for producing a diphenylalkane which comprises reacting at a temperature of

from about 100° to about 250° C. in the presence of aluminum a gas containing free oxygen and an aromatic hydrocarbon having an alkyl group of at least two carbon atoms and containing at least one hydrogen atom combined with the carbon atom attached to the benzene ring.

3. A process for producing a nuclearly chlorinated diphenylalkane which comprises reacting at a temperature of from about 100° to about 250° C. in the presence of aluminum a gas containing free oxygen and a nuclearly chlorinated alkyl aromatic hydrocarbon in which said alkyl group contains at least two carbon atoms and at least one hydrogen atom combined with the carbon atom attached to the benzene ring.

4. A process for producing a diphenyl alkane which comprises reacting a gas containing free oxygen and a benzene hydrocarbon having an alkyl group of at least two carbon atoms and containing at least one hydrogen atom combined with the carbon atom attached to the benzene ring at a temperature of from about 100° to about 250° C. in the presence of aluminum.

5. A process for producing a diphenyl alkane which comprises reacting air and a benzene hydrocarbon having an alkyl group of at least two carbon atoms and containing at least one hydrogen atom combined with the carbon atom attached to the benzene ring at a temperature of from about 125° to about 200° C. in the presence of aluminum.

6. A process for producing a diphenyl alkane which comprises reacting a gas containing free oxygen and a benzene hydrocarbon having an alkyl group of at least two carbon atoms and containing at least one hydrogen atom combined with the carbon atom attached to the benzene ring at a temperature of from about 100° to about 250° C. in the presence of magnesium.

7. A process for producing a diphenyl alkane which comprises reacting air and a benzene hydrocarbon having an alkyl group of at least two carbon atoms and containing at least one hydrogen atom combined with the carbon atom attached to the benzene ring at a temperature of from about 125° to about 200° C. in the presence of magnesium.

8. A process for producing a nuclearly chlorinated diphenyl alkane which comprises reacting a gas containing free oxygen and a nuclearly chlorinated alkyl benzene hydrocarbon in which said alkyl group contains at least two carbon atoms and at least one hydrogen atom combined with the carbon atom attached to the benzene ring at a temperature of from about 100° to about 250° C. in the presence of aluminum.

9. A process for producing a nuclearly chlorinated diphenyl alkane which comprises reacting air and a nuclearly chlorinated alkyl benzene hydrocarbon in which said alkyl group contains at least two carbon atoms and at least one hydrogen atom combined with the carbon atom attached to the benzene ring at a temperature of from about 125° to about 200° C. in the presence of aluminum.

HERMAN PINES.
BRUNO KVETINSKAS.
VLADIMIR N. IPATIEFF.

REFERENCES CITED

The following references are of record in the file of this patent:

FOREIGN PATENTS

Number	Country	Date
646,701	Germany	June 23, 1937

OTHER REFERENCES

Berkman et al.: Catalysis, page 803 (1940).

Groggins: Unit Processes in Organic Synthesis, page 480 (1947), 3rd edition, McGraw-Hill Publishing Co., New York, N. Y.