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PROCESS FOR THE CONDENSATION OF AN ARYLALKANE IN THE PRESENCE OF LEAD ALKYL

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8 Claims. (Cl. 260—668)

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This invention relates to a process for condensing a hydrocarbon containing a replaceable hydrogen atom. More particularly, the process relates to the condensation of alkyl aromatic hydrocarbons to form aromatic hydrocarbons of higher molecular weights.

An object of this invention is to condense a hydrocarbon containing an alkyl group in the presence of a metal alkyl.

An additional object of this invention is to condense an alkyl aromatic hydrocarbon in the presence of a lead alkyl.

Another object of this invention is to condense an alkyl benzene hydrocarbon in the presence of a lead alkyl.

A further object of this invention is to produce a diarylalkane by reacting an arylalkane in the presence of lead tetraethyl.

One specific embodiment of the present invention relates to a process for producing a polyarylalkane which comprises condensing an arylalkane in the presence of a lead alkyl.

Another embodiment of this invention relates to a process for producing a polyphenylalkane which comprises reacting in the presence of a lead tetra-alkyl, a benzene hydrocarbon having an alkyl group represented by the formula:



wherein R and R′ represent at least one member of the group consisting of a hydrogen atom and an alkyl group.

A further embodiment of this invention relates to a process for producing a diphenylalkane which comprises reacting in the presence of a lead alkyl, an alkyl benzene hydrocarbon in which the alkyl group is represented by the formula:

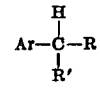


wherein R and R′ represent at least one member of the group consisting of a hydrogen atom and an alkyl group.

Hydrocarbons which are condensed by my process to form hydrocarbons of higher molecular weights include paraffins, olefins, naphthenes, and aromatics each containing an alkyl group which has at least one replaceable hydrogen atom. Such hydrocarbons react in the presence of a lead alkyl to split out hydrogen and effect a condensation of two fragments resulting from the loss of hydrogen from the hydrocarbon being treated.

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Aromatic hydrocarbons particularly suitable for use in my process have an alkyl group in which a hydrogen atom is combined with a carbon atom adjacent to the aromatic ring. Such hydrocarbons may be represented by the general formula:

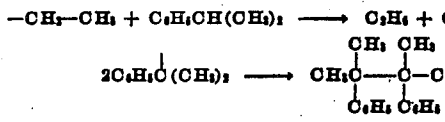


wherein Ar represents an aromatic ring and R and R′ represent at least one member of the group consisting of a hydrogen atom and an alkyl group. Benzene hydrocarbons particularly suitable for my process comprise toluene, ethylbenzene, isopropyl benzene, and other alkyl benzene hydrocarbons of higher molecular weights.

The above indicated alkyl aromatic hydrocarbons and particularly the alkyl benzene hydrocarbons are reacted singly or in admixture with one another in the presence of a lead alkyl to form higher boiling condensation products generally derived by the combination of 2 molecular proportions of the alkyl aromatic hydrocarbon and the splitting out of hydrogen. The process is carried out in batch or continuous types of treatment at a temperature of from about 0° to about 300° C. for a time sufficient to decompose the added lead alkyl compound and to form condensation products from a portion of the aromatic hydrocarbon or aromatic hydrocarbon mixture undergoing treatment. The formation of aromatic condensation products takes place slowly when a mixture of an alkyl benzene hydrocarbon and a lead alkyl is exposed to light at a temperature of about 0° to about 100° C. but preferably of from about 20° to about 40° C. during a relatively long period of time. Also, the condensation can be effected in a relatively short time by heating the aromatic hydrocarbon and metal alkyl in an autoclave at a temperature up to about 300° C. After the reaction has been carried out, the reaction mixture is filtered to separate solid decomposition products of the metal alkyl from a solution of the reaction product in the excess of alkyl aromatic hydrocarbon charged to the process. The excess of unconverted alkyl aromatic hydrocarbon is then distilled and separated from the higher boiling condensation products comprising essentially a polyphenylalkane hydrocarbon or mixture of polyphenylalkane hydrocarbons.

Although the mechanism of the condensation reaction is not known completely, it seems probable that the reaction proceeds through the formation of free radicals produced during the ac-

celerated decomposition of the metal alkyl such as lead tetraethyl. Although these concepts should not be misconstrued to limit the broad scope of the invention, it is believed that lead tetraethyl, for example, decomposes to give free ethyl radicals and that these react with the hydrocarbon, such as cumene, as illustrated in the following equation:



The following examples are given to indicate results obtained in this process, but these data should not be misconstrued to limit the broad scope of the invention.

Example I

105 grams of cumene, 6.2 grams of lead tetraethyl, and 3.8 grams of ethylene dibromide (10 grams of "ethyl fluid") were mixed in a 200 cc. colorless glass bottle, the bottle was tightly corked, and exposed to autumn and winter sunlight at about 25° C. during a period of 137 days. The reaction mixture was then filtered to remove precipitated material formed from the lead tetraethyl and the excess of cumene was removed by distillation from a residue which crystallized on cooling. This residue purified by recrystallization from pentane yielded about 1.5 grams of pure 2,3-dimethyl-2,3-diphenylbutane.

Example II

120 cc. of toluene was mixed with 18 grams of "ethyl fluid" (consisting of 11 grams of lead tetraethyl and 7 grams of ethylene dibromide) and the resultant solution in a clear glass bottle was exposed to spring and summer sunlight at 25° to 40° C. during a period of about 200 days after which the reaction mixture was filtered to remove precipitated material. Toluene was distilled from the filtered hydrocarbon material, leaving a residue of about 4 grams. The residue which was dissolved in pentane and cooled yielded a crystalline precipitate (2 grams) which melted at 50–51° C., the melting point of dibenzyl. This crystalline material did not depress the melting point when mixed with an authentic sample of dibenzyl. The remainder of the residue apparently contained an additional quantity of dibenzyl and also higher condensation products which probably resulted from reaction with the —CH_2— groups of the initially formed dibenzyl.

Example III

When the procedure of Example II was repeated on a mixture of 200 cc. of triptane, 22 grams of lead tetraethyl and 14 grams of ethylene dibromide, only about 2 grams of residue remained after distilling off the unreacted triptane. Examination of this higher boiling residue of infra red methods indicated that it was a mixture of highly branched hydrocarbons containing quaternary carbon atoms.

Example IV

300 cc. of ethyl benzene, 22 grams of lead tetraethyl, and 14 grams of ethylene dibromide were mixed and the resultant solution was exposed to spring and summer sunlight during a period of six months. At the end of this time, the precipitated material formed by decomposition of the lead tetraethyl was removed by filtration, the unreacted ethyl benzene was distilled from the reaction product, and the residue was permitted to crystallize. After recrystallization from pentane, the residue yielded 7 grams of crystals melting at 122–123° C., thus corresponding closely in melting point to that of 2,3-diphenylbutane. In addition, 6 grams of non-crystalline material was also present in the residue, this material probably being formed by further reaction of 2,3-diphenylbutane.

In this and in the preceding examples, ethylene dibromide was present because "ethyl fluid" was added rather than pure lead tetraethyl.

Example V

200 cc. of cumene and 2 cc. of pure lead tetraethyl (containing no ethylene dibromide) were placed in a glass liner for a rotatable steel autoclave of 850 cc. capacity. The glass liner and its contents were sealed in the autoclave, nitrogen was added to 25 atmospheres pressure, and the charged autoclave was rotated and heated at 250° C. for 7 hours. The autoclave was then cooled, the gas (mainly nitrogen) was released therefrom, and the glass liner containing the reaction product was removed from the autoclave. During the run the lead tetraethyl had decomposed, forming a solid on the sides of the glass liner. The liquid product was filtered from the decomposition products of the lead tetraethyl and the unreacted cumene was recovered by distillation, leaving a solid residue of 3.3 grams which was identified as 2,3-dimethyl-2,3-diphenylbutane by a mixed melting point determination with an authentic sample of 2,3-dimethyl-2,3-diphenylbutane.

The foregoing specification and examples indicate results obtained in my process, but these data should not be misconstrued to limit the broad scope of my invention.

I claim as my invention:

1. A process for producing a polyarylalkane which comprises contacting an arylalkane having a hydrogen atom attached to a carbon atom adjacent to the aromatic ring with a lead alkyl, in which all valences of the lead atom are satisfied by alkyl groups, at a temperature of from about 0° C. to about 300° C. for a time sufficient to decompose said lead alkyl and to form a condensation product from at least two molecular portions of said arylalkane, and thereafter separating from the reaction mixture the solid decomposition products of said lead alkyl.

2. The process of claim 1 wherein said lead alkyl comprises lead tetraethyl.

3. A process for producing a diarylalkane which comprises contacting an arylalkane having a hydrogen atom attached to a carbon atom adjacent to the aromatic ring with a lead alkyl, in which all valences of the lead atom are satisfied by alkyl groups, at a temperature of from about 0° C. to about 300° C. for a time sufficient to decompose said lead alkyl and to form a condensation product from two molecular portions of said arylalkane, and thereafter separating from the reaction mixture the solid decomposition products of said lead alkyl.

4. The process of claim 3 wherein said lead alkyl comprises lead tetraethyl.

5. A process for producing dibenzyl which comprises contacting toluene with lead tetraethyl at a temperature of from about 0° C. to about 300° C. for a time sufficient to decompose said lead tetraethyl and to condense two molecular proportions of said toluene, and thereafter sep-

arating from the reaction mixture the solid decomposition products of said lead tetraethyl.

6. A process for producing 2,3-diphenylbutane which comprises contacting ethylbenzene with lead tetraethyl at a temperature of from about 0° C. to about 300° C. for a time sufficient to decompose said lead tetraethyl and to condense two molecular proportions of said ethylbenzene, and thereafter separating from the reaction mixture the solid decomposition products of said lead tetraethyl.

7. A process for producing 2,3-dimethyl-2,3-diphenylbutane which comprises contacting cumene with lead tetraethyl at a temperature of from about 0° C. to about 300° C. for a time sufficient to decompose said lead tetraethyl and to condense two molecular proportions of said cumene, and thereafter separating from the reaction mixture the solid decomposition products of said lead tetraethyl.

8. The process of claim 1 further characterized in that the reaction is carried out under the influence of actinic light.

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