Patented Nov. 9, 1943 2,333,866

UNITED STATES PATENT OFFICE

2,333,866

TREATMENT OF HYDROCARBONS

Vasili I. Komarewsky, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

No Drawing. Application October 19, 1942, Serial No. 462,591

15 Claims. (Cl. 260—671)

This is a continuation-in-part of my co-pending application Serial No. 273,679, filed May 15, 1939.

This invention relates to a process for the manufacture of derivatives of aromatic hydrocarbons, particularly those formed by replacing hydrogen atoms of the aromatic ring with aliphatic hydrocarbon radicals.

The value of the various aromatic hydrocarbons as raw materials for the manufacture of chemical derivatives is well known. These serve as starting materials for the manufacture of dyestuffs, explosives, disinfectants, solvents, fuels, etc.

In the production of aromatic hydrocarbons by the destructive distillation of coal or of other hydrocarbon mixtures such as those constituting the various fractions of petroleum, there are normally produced in the mono-nuclear series preponderating yields of benzene and of its closely related homologs such as toluene and the xylenes, these latter being the mono- and di-methyl derivatives of benzene, respectively. The products of such destructive distillations include practically no benzene homologs containing aliphatic radicals of higher molecular weights such as, for example ethyl benzene, propyl benzene, etc. While the present process may be employed to produce any alkyl derivatives of benzene, excluding the methyl derivatives, it is particularly applicable to the production of the higher alkyl derivatives.

To review briefly the alkylation art with the object of distinguishing it from the process of the present invention, it may be stated that one of the best known methods consists in using olefins to treat aromatics in the presence of sulfuric acid. The efficiency of the reaction of the above character in producing alkylated benzenes is limited to a considerable extent by the tendency of sulfuric acid to promote polymerization of the olefins rather than the simple addition of the olefin to the aromatic nucleus. Also, sulfuric acid has a tendency to sulfonate the aromatics and to oxidize the olefinic hydrocarbons involved, thus producing undesirable by-products, these sometimes being of the character of a heavy tar.

It is also known in the art to employ metal halides such as, for example, aluminum chloride for catalyzing the reactions of olefins with aromatics. Metal halide catalysts tend to foster polymerization of oelfins to a great extent and frequently lead to the formation of sludges consisting of compounds formed by the addition of olefins to the metal halide. There is also considerable tendency to carbonization if elevated temperatures are employed and the reactions are difficult to control so as to produce predominantly a single product such as a mono-alkyl derivative, since there is usually concurrent formation of di-, tri, and poly-alkylated derivatives.

Also, it is known that alkylated aromatic hydrocarbons may be formed by reacting a mixture of paraffinic and aromatic hydrocarbons in the presence of a phosphoric acid catalyst at a temperature of from about 700° to about 900° F. under a pressure up to about 128 atmospheres. This method involves the use, as catalyst, of a corrosive acid under relatively severe conditions of temperature and pressure.

One specific embodiment of the present invention comprises a process for manufacturing alkylated aromatic hydrocarbons by reacting an aromatic hydrocarbon and a paraffinic hydrocarbon containing at least 4 carbon atoms per molecule in the presence of sulfuric acid at a temperature of from about —25° to about 100° C.

In carrying out the process of the present invention, a paraffinic and an aromatic hydrocarbon are reacted in the presence of from about 10 to about 100% by weight of sulfuric acid of from about 60 to about 100% concentration. When a liquid paraffinic hydrocarbon is so utilized, the mixture containing the proportions of paraffinic and aromatic hydrocarbons necessary for producing high yields of the desired alkylated product is agitated with the sulfuric acid catalyst in a rotating autoclave or other suitable reactor maintained at a temperature of from about —25° to about 100° C. and under a pressure of from about 1 to about 40 atmospheres. Also, the mixture of hydrocarbons and acid may be pumped through chambers suitably maintained at the desired temperature to allow continuous operation, reliance being placed on turbulence due to flow or developed by mechanical mixing devices to assure effective contact.

If an aromatic hydrocarbon is to be alkylated by a butane, which is generally a much more active alkylating agent than methane, ethane, or propane, the gaseous butane may be charged under pressure into a chamber or autoclave containing the aromatic hydrocarbon and the sulfuric acid catalyst, whereupon the chamber or autoclave is shaken or otherwise agitated and maintained at a temperature sufficient to effect alkylation. The pressure employed in such an alkylation reaction is usually from about 1 to about 50 atmospheres.

Reactions of alkylation may be brought about

also between a normally gaseous paraffin and liquid aromatics in chambers by injecting the gaseous paraffin into the continuously flowing stream of aromatic hydrocarbon and sulfuric acid. This and other methods of contacting, such as by atomizing a liquid aromatic hydrocarbon and sulfuric acid in proper proportions into an atmosphere of the gaseous paraffin hydrocarbon will suggest themselves to those familiar with these types of industrial operations. Arrangements may be made to pass mixtures of the aromatics and paraffins upwardly countercurrent to descending streams of sulfuric acid in towers filled with relatively inert fragmentary material, such as crushed silica, quartz, porcelain, etc., in order to insure effective contact.

The temperature and pressure conditions under which alkylation reactions are to be carried out most effectively will generally vary with each combination of aromatic and paraffin hydrocarbons which may be employed, and with the amount of sulfuric acid catalyst used.

The types of reactions which occur in the present process are sharply differentiated from those taking place when olefins are employed to alkylate aromatics to produce alkyl aromatic hydrocarbons. The present process also differs from another previously known process relating to the alkylation of an aromatic hydrocarbon with a cycloparaffin, a hydrocarbon of the class having the empirical formula C_nH_{2n} and thereby isomeric with the mono-olefins which also have the empirical formula C_nH_{2n}. In contrast to the olefins and cycloparaffins, the paraffins are saturated hydrocarbons with the empirical formula C_nH_{2n+2}. In the present instance, the paraffins may be considered as undergoing decomposition in the presence of sulfuric acid to form active fragments or radicals which then unite with the aromatics to form the desired alkyl derivatives. Hydrogen and/or paraffins are sometimes also formed during the alkylation treatment. In a sense, the reactions involved may be regarded as condensation reactions since there is often some elimination of hydrogen and formation of lower boiling hydrocarbons.

The process thus utilizes paraffins of generally relatively low activity to combine with and alkylate aromatic hydrocarbons. The practical utility of the process is the fact that various paraffins and paraffin mixtures may be so employed instead of the more reactive olefins which heretofore were the alkylating agents usually employed.

The following example is given to illustrate the nature of the reactions involved and the results obtainable by the use of the process, although the generally broad scope of the invention is not limited by the data presented.

One hundred forty volumes of a mixture of equal parts by weight of benzene and isooctane, comprising essentially 2,2,4-trimethyl pentane, was stirred at room temperature for ten hours with 100 volumes of 100% sulfuric acid. The resultant liquid contained 60% of hydrocarbons boiling above benzene and consisted mainly of butyl benzenes and other alkylation products. The gaseous product of the reaction contained relatively small amounts of butane.

The nature of the present invention and of its commercial utility can be seen from the specification and the example given, although neither section is intended to unduly limit its generally broad scope.

I claim as my invention:

1. A process for producing alkylated aromatic hydrocarbons which comprises reacting an aromatic hydrocarbon and a paraffinic hydrocarbon under alkylating conditions in the presence of sulfuric acid and recovering the alkylated aromatic hydrocarbons thus formed.

2. A process for producing alkylated aromatic hydrocarbons which comprises reacting an aromatic hydrocarbon and a paraffinic hydrocarbon containing at least 4 carbon atoms per molecule under alkylating conditions in the presence of sulfuric acid and recovering the alkylated aromatic hydrocarbons thus formed.

3. A process for producing alkylated aromatic hydrocarbons which comprises reacting an aromatic hydrocarbon and a paraffinic hydrocarbon containing at least 4 carbon atoms per molecule at a temperature of from about −25° to about 100° C. in the presence of sulfuric acid and recovering the alkylated aromatic hydrocarbons thus formed.

4. A process for producing alkylated aromatic hydrocarbons which comprises reacting an aromatic hydrocarbon and a paraffinic hydrocarbon containing at least 4 carbon atoms per molecule at a temperature of from about −25° to about 100° C. in the presence of a sulfuric acid catalyst of from about 60 to about 100% concentration and recovering the alkylated aromatic hydrocarbons thus formed.

5. A process for producing alkylated aromatic hydrocarbons which comprises reacting an aromatic hydrocarbon and a paraffinic hydrocarbon containing at least 4 carbon atoms per molecule at a temperature of from about −25° to about 100° C. under a pressure of from about 1 to about 40 atmospheres in the presence of sulfuric acid and recovering the alkylated aromatic hydrocarbons thus formed.

6. A process for producing alkylated aromatic hydrocarbons which comprises reacting an aromatic hydrocarbon and a butane under alkylating conditions in the presence of sulfuric acid and recovering the alkylated aromatic hydrocarbons thus formed.

7. A process for producing alkylated aromatic hydrocarbons which comprises reacting an aromatic hydrocarbon and a butane at a temperature of from about −25° to about 100° C. under a pressure of from about 1 to about 40 atmospheres in the presence of sulfuric acid and recovering the alkylated aromatic hydrocarbons thus formed.

8. A process for producing alkylated aromatic hydrocarbons which comprises reacting an aromatic hydrocarbon and a normally liquid paraffin under alkylating conditions in the presence of sulfuric acid and recovering the alkylated aromatic hydrocarbons thus formed.

9. A process for producing alkylated aromatic hydrocarbons which comprises reacting an aromatic hydrocarbon and a normally liquid paraffin at a temperature of from about −25° to about 100° C. under a pressure of from about 1 to about 40 atmospheres in the presence of sulfuric acid and recovering the alkylated aromatic hydrocarbons thus formed.

10. A process for producing alkylated aromatic hydrocarbons which comprises treating a mixture of aromatic and paraffinic hydrocarbons with sulfuric acid at a temperature of from about −25° to about 100° C. under a pressure of from about 1 to about 40 atmospheres and recover-

ing the alkylated aromatic hydrocarbons thus formed.

11. A process for alkylating an aromatic hydrocarbon of the benzene series which comprises treating said aromatic hydrocarbon and a paraffin containing at least 4 carbon atoms per molecule with sulfuric acid at a temperature of from about —25° to about 100° C. under a pressure of from about 1 to about 40 atmospheres and recovering the alkylated aromatic hydrocarbons thus formed.

12. A process for alkylating an aromatic hydrocarbon of the benzene series which comprises treating said aromatic hydrocarbon and a paraffin containing at least 4 carbon atoms per molecule with sulfuric acid of from about 60 to about 100% concentration at a temperature of from about —25° to about 100° C. under a pressure of from about 1 to about 40 atmospheres and recovering the alkylated aromatic hydrocarbons thus formed.

13. A process for alkylating an aromatic hydrocarbon of the benzene series which comprises treating said aromatic hydrocarbon and a normally liquid paraffinic hydrocarbon with sulfuric acid of from about 60 to about 100% concentration at a temperature of from about —25° to about 100° C. under a pressure of from about 1 to about 40 atmospheres and recovering the alkylated aromatic hydrocarbons thus formed.

14. A process for alkylating benzene which comprises treating benzene and a normally liquid paraffin with sulfuric acid of from about 60 to about 100% concentration at a temperature of from about —25° to about 100° C. under a pressure of from about 1 to about 40 atmospheres and recovering the alkylated aromatic hydrocarbons thus formed.

15. A process for alkylating benzene which comprises treating benzene and isooctane with sulfuric acid of from about 60 to about 100% concentration at a temperature of from about —25° to about 100° C. under a pressure of from about 1 to about 40 atmospheres and recovering the alkylated aromatic hydrocarbons thus formed.

VASILI I. KOMAREWSKY.