United States Patent Office 2,742,516 Patented Apr. 17, 1956

2,742,516

ALKYLATION OF HYDROCARBONS

Abraham Schneider, Philadelphia, Pa., assignor to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

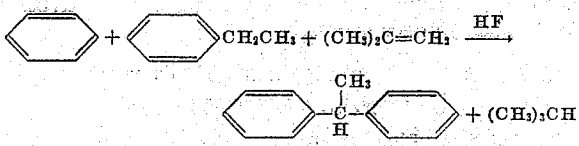
No Drawing. Application September 22, 1953, Serial No. 381,754

11 Claims. (Cl. 260—668)

This invention relates to the alkylation of aromatic hydrocarbons with monoalkyl benzenes, and more specifically relates to the alkylation of certain mononuclear aromatic hydrocarbons with monoalkyl benzenes having at least 2 carbon atoms in the alkyl group.

One specific embodiment of the invention relates to a process for producing a diarylalkane hydrocarbon which comprises reacting under specific conditions, as hereinafter defined, a mononuclear aromatic hydrocarbon, such as benzene, with a monoalkyl benzene having at least two carbon atoms in the alkyl substituent, such as ethylbenzene, by subjecting a mixture thereof to the action of a tertiary olefin and hydrogen fluoride. It has been found that under these conditions the monoalkyl benzene alkylates the mononuclear aromatic to form a diarylalkane hydrocarbon, and that alkylation of either aromatic reactant with the tertiary olefin is not observed to any substantial extent.

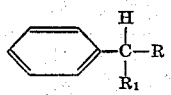
In order to illustrate the process of the invention, isobutylene is added to an admixture of benzene, ethylbenzene, and hydrogen fluoride while maintaining the temperature of the reaction mixture within the range of from 100° C. to 185° C. The reaction product of benzene and ethylbenzene, 1,1-diphenylethane, is formed and can be recovered from the reaction mixture by distillation. Under optimum conditions of reaction, substantially no tertiary butylbenzene or tertiary butylethylbenzene is observed. This reaction is illustrated by the following equation:



In my copending patent application, Serial No. 381,752, filed September 22, 1953, the dimerization of mononuclear aromatic hydrocarbons, such as ethylbenzene, under the influence of a tertiary olefin and hydrogen fluoride is described. In the presence of benzene and under the reaction conditions herein defined, the dimerization reaction of Serial No. 381,752 is substantially completely suppressed so that the dimer of the monoalkyl aromatic in the present process does not constitute a product of the reaction.

Benzene is the preferred mononuclear aromatic hydrocarbon to employ. The benzene nucleus may be substituted with from 1 to 4 methyl groups and good results obtained therewith, for example, toluene, the xylenes, and the trimethyl benzenes, such as mesitylene, give good results.

Monoalkyl benzenes which can be employed in the process of the invention have the formula



wherein R is an alkyl radical or a cycloalkyl radical having

from 1 to 20 carbon atoms, and wherein R_1 is an alkyl radical or a cycloalkyl radical having from 1 to 20 carbon atoms, or a hydrogen atom. The alkyl benzene thus has at least two carbon atoms in the alkyl group and at least one hydrogen atom is attached to the carbon atom of the alkyl group which is joined to the aromatic nucleus. Ethylbenzene and cumene (isopropyl benzene) are preferred reactants in the present process. Other monoalkyl benzenes which may be employed include, for example, n-propylbenzene, secondary butybenzene, secondary amylbenzene, phenylcyclohexylmethane, 1-phenyl-2-cyclohexylethane and the like. The monoalkyl benzene reactant is preferably substantially free of other hydrocarbons, and best results are obtained when the presence of other hydrocarbons is maintained below 10%. However, hydrocarbons which do not react under the conditions employed, such as normal paraffins, may be present to an extent of about 40% without adversely affecting the reaction. Isoparaffins react under the conditions employed in the process, and hence they should not be present to an appreciable extent.

By "tertiary olefins," as used herein, is meant a hydrocarbon having an olefinic double bond and at least one tertiary carbon atom. It is preferred to employ a tertiary olefin wherein the branched chain is attached to the unsaturated carbon atom. Tertiary olefins which give good results include, for example, isobutylene, 2-methylbutene-2; 2-methylbutene-1; 2-methylpentene-2; 3-ethylpentene-2; 1-methylcyclohexene; 4-methylcyclohexene; and homologues and isomers thereof.

The mole ratio of tertiary olefin to monoalkyl benzene is preferably maintained within the range of from 0.1:1 to 1:1. Where the mole ratio is about 0.1:1, a relatively high yield of the diarylalkane based on conversion is obtained, while at higher mole ratios a higher total conversion is obtained. The quantity of hydrogen fluoride to employ is not critical but is advantageously maintained in excess. A mole ratio of hydrogen fluoride to tertiary olefin of from 1:1 to 20:1 is suitable.

It is preferred to employ an excess of the mononuclear aromatic hydrocarbon. A mole ratio of mononuclear aromatic hydrocarbon to monoalkyl benzene of from 0.5:1 to 10:1 is suitable and excellent results are obtained when the mole ratio is from 1:1 to 2:1.

It is essential to the successful operation of the present process that the temperature of reaction be maintained at least as high as 100° C. At temperatures of below 100° C., alkylation of the monoalkyl aromatic by the tertiary olefin is substantially the only reaction obtained, although disproportion is also observed at temperatures only slightly below 100° C. It is preferred to employ temperatures below 185° C. since at higher temperatures a wide variety of products is obtained due to reactions of the product under the influence of a catalyst. Accordingly, it is essential that the temperature of reaction be maintained at least as high as 100° C. and preferably is maintained at a temperature of not above 185° C. The pressure to employ is not critical so long as reaction is maintained in the liquid phase. In general the pressure will vary from atmospheric up to about 500 p. s. i. Time is also not considered a critical variable, it being apparent that sufficient time should be allowed to obtain a substantial yield of the desired product. The usual time of reaction will be from 10 minutes to about 5 hours.

In carrying out the process of the invention, the tertiary olefin and hydrogen fluoride should not be contacted except in the presence of both the monoalkyl benzene and the mononuclear aromatic. A preferred method of performing the process is to admix the monoalkyl benzene and the mononuclear aromatic with hydrogen fluoride, and to then add tertiary olefin, with agitation, to the mixture.

As above described, patent application Serial No. 381,752 describes and claims the process for the dimerization of monoalkyl benzenes. For example, by adding 57.5 grams (1.03 moles) of isobutylene over a period of 90 minutes to 212 grams (2.01 moles) of ethylbenzene and 155 grams (7.75 moles) of hydrofluoric acid, the temperature being maintained at a minimum of 100° C., there was obtained 33 grams (0.057 mole) of 1-phenyl-1-p-ethylphenylethane, the dimer of ethylbenzene. In accordance with the process of the present invention, benzene is included in the reaction mixture preferably in at least an equal molar quantity with the ethylbenzene. In the presence of benzene, the formation of the dimer of ethylbenzene is suppressed and instead there is formed the alkylation product of benzene and ethylbenzene, namely, 1,1-diphenylethane, the quantity formed being about the same as that obtained for the dimer of ethylbenzene in Serial No. 381,752.

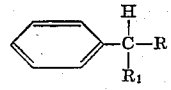
At the minimum temperature of 100° C., a small amount of the alkylation product of benzene and tertiary olefin may be observed, while at higher temperatures, say about 125° C., substantially none of this product is obtained in the reaction.

The diarylalkane products of the present process can be used as lubricating oil additives, intermediates in the preparation of detergents, for the synthesis of other compounds, and the like.

When monoalkyl benzenes other than ethylbenzene and when mononuclear aromatics other than benzene are employed, substantially equivalent results are obtained. Also other olefins, as above described, may be substituted for isobutylene and equivalent results obtained.

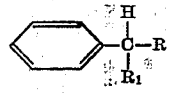
The invention claimed is:

1. Process of alkylation which comprises reacting a mononuclear aromatic hydrocarbon having from 0 to 4 methyl groups attached to the aromatic nucleus with a monoalkyl benzene having the formula



wherein R is a material selected from the group consisting of alkyl radicals having from 1 to 20 carbon atoms and cycloalkyl radicals having from 1 to 20 carbon atoms, and wherein R_1 is a material selected from the group consisting of a hydrogen atom, alkyl radicals having from 1 to 20 carbon atoms and cycloalkyl radicals having from 1 to 20 carbon atoms in the presence of a tertiary olefin and hydrogen fluoride, said reaction being performed in liquid phase at a temperature of from 100° C. to 185° C.

2. Process of alkylating benzene with a monoalkyl benzene having the formula



wherein R is a material selected from the group consisting of alkyl radicals having from 1 to 20 carbon atoms and cycloalkyl radicals having from 1 to 20 carbon atoms, and wherein R_1 is a material selected from the group consisting of a hydrogen atom, alkyl radicals having from 1 to 20 carbon atoms and cycloalkyl radicals having from 1 to 20 carbon atoms which comprises reacting in liquid phase at a temperature of from 100° C. to 185° C., benzene with said monoalkyl benzene in the presence of a tertiary olefin having from 4 to 7 carbon atoms and hydrogen fluoride.

3. Process according to claim 2 wherein said monoalkyl benzene is ethylbenzene.

4. Process according to claim 2 wherein said monoalkyl benzene is cumene.

5. Process according to claim 2 wherein said monoalkyl benzene is n-propylbenzene.

6. Process according to claim 2 wherein said monoalkyl benzene is secondary butylbenzene.

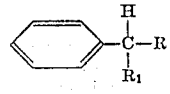
7. Process according to claim 2 wherein said monoalkyl benzene is secondary amylbenzene.

8. Process for the preparation of 1,1-diphenylethane which comprises contacting an admixture of benzene and ethylbenzene with a tertiary olefin and hydrogen fluoride, said contacting being performed in liquid phase at a temperature of 100° C. to 185° C. and separating 1,1-diphenylethane from the reaction mixture.

9. Process according to claim 8 wherein the tertiary olefin is added to an admixture of benzene, ethylbenzene, and hydrogen fluoride.

10. Process according to claim 9 wherein the tertiary olefin is osobutylene.

11. Process of alkylating toluene with a monoalkyl benzene having the formula



wherein R is a material selected from the group consisting of alkyl radicals having from 1 to 20 carbon atoms and cycloalkyl radicals having from 1 to 20 carbon atoms, and wherein R_1 is a material selected from the group consisting of a hydrogen atom, alkyl radicals having from 1 to 20 carbon atoms and cycloalkyl radicals having from 1 to 20 carbon atoms which comprises reacting in liquid phase at a temperature of from 100° C. to 185° C., toluene with said monoalkyl benzene in the presence of a tertiary olefin and hydrogen fluoride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,671,815 Pines et al. ---------- Mar. 9, 1954