

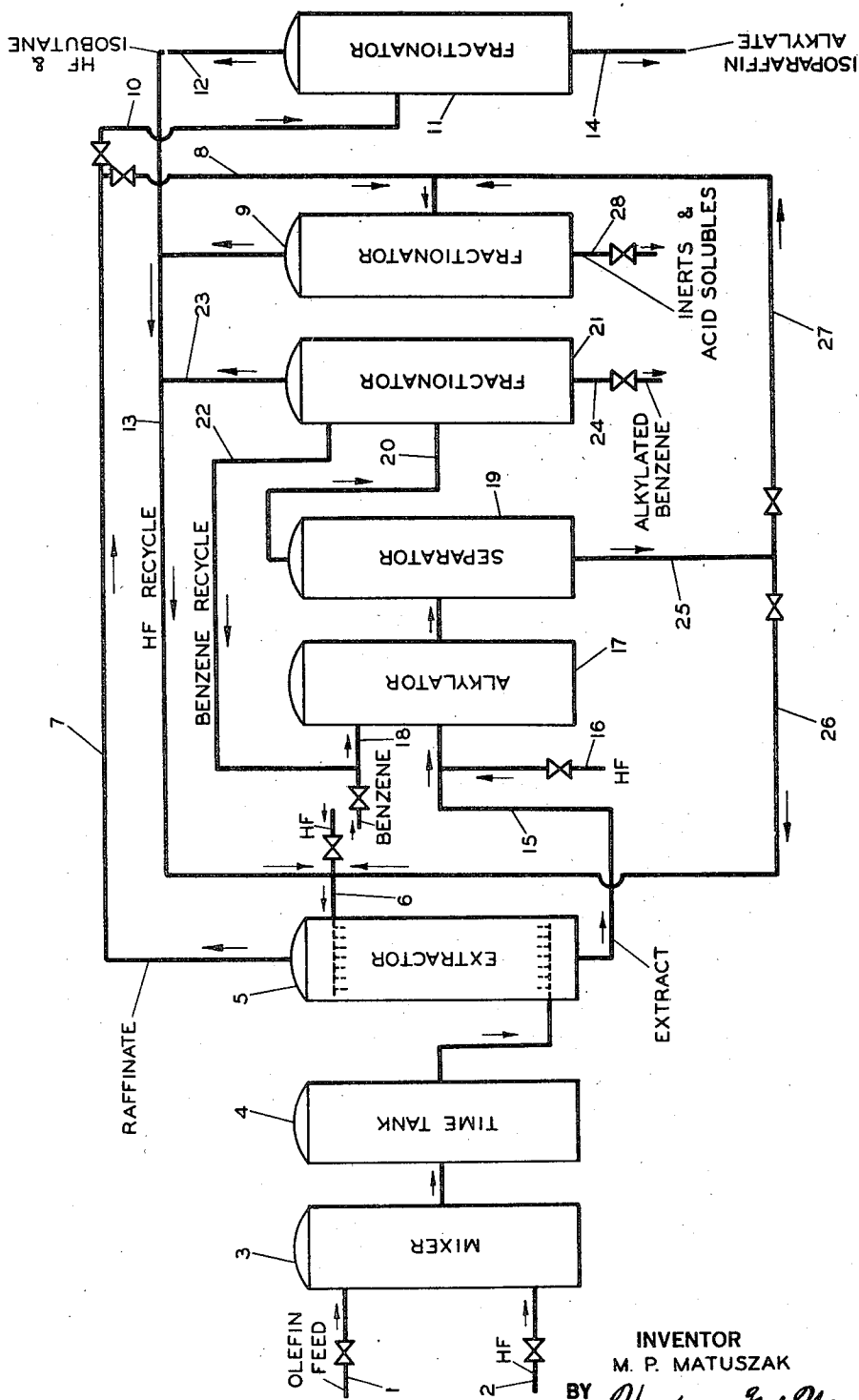
Dec. 14, 1948.

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2,456,435

ALKYLATION PROCESS

Filed Aug. 6, 1945



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2,456,435

ALKYLATION PROCESS

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Application August 6, 1945, Serial No. 609,214

20 Claims. (Cl. 260—345)

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This invention relates to an alkylation process and more particularly to an improved process for reacting a low-boiling aliphatic olefin with an alkylatable cyclic organic compound to produce alkyl derivatives thereof wherein hydrogen atoms on the ring are replaced by alkyl groups corresponding to the olefin. Still more particularly it relates to a process for the alkylation of benzene, toluene or other aromatic compound, furan, derivatives of furan, cycloparaffins, and any other cyclic organic compounds which are capable of being alkylated by replacement of hydrogen on the ring with alkyl groups.

This application is a continuation-in-part of my prior and copending application, Ser. No. 467,874, filed December 4, 1942, now Patent No. 2,387,162.

In present-day acid-catalyzed alkylation processes, it is necessary, for obtaining optimum results, to limit the proportions of inert diluents in the feed to the alkylating zone. Diluents in the feed reduce the maximum production capacity of alkylating equipment and, if present in high proportion, cause reductions in yield and quality of the product. Although diluents are sometimes removed from feeds by preliminary fractional distillation, such distillation in many instances is not economically feasible, particularly in the utilization of olefinic streams that contain only a few per cent of olefin. The present process advantageously effects removal of inerts without such preliminary distillation.

The principal object of the present invention is to provide an improved process for the alkylation of an alkylatable cyclic organic compound with a low-boiling aliphatic olefin. Another object is to provide such a process for the alkylation of aromatic hydrocarbons. Another object is to provide such a process for the alkylation of a so-called "superaromatic" such as furan. Another object is to provide such a process wherein the olefin employed is in admixture with large proportions of inert materials especially the corresponding paraffin. Another object is to provide such a process wherein the olefin is an isoolefin such as isobutylene and is in admixture with large proportions of the corresponding isoparaffin such as isobutane, as for example, in the case where the olefin-containing feed is prepared by the catalytic dehydrogenation of isobutane followed by known treatment to segregate the C₄ fraction. Another object is to minimize the alkylation of isoparaffin in a process of the type mentioned in the preceding sentence whereby consumption of olefin by alkylation of isoparaffin is kept at a min-

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imum and a maximum of the olefin contained in the feed is converted to the desired principal product, namely, alkylate of the cyclic organic compound. Another object is to provide a process as just outlined wherein the isoparaffin present in the feed is eliminated ahead of the alkylation zone wherein alkylation of the cyclic organic compound takes place, said elimination removing both the isoparaffin present as such and the small proportion thereof which is inevitably alkylated prior to the alkylation zone proper. Another object is to provide a process as in the foregoing wherein the by-product higher isoparaffin, usually isooctane, formed by unavoidable alkylation of isoparaffin prior to the main alkylation zone is separately recovered in a novel and advantageous manner. Another object is to provide a process which accomplishes the foregoing objects in a simple, economical manner requiring a minimum of control and which is readily controlled to effect the desired results to an optimum extent.

Many other aims, objects and advantages of the present invention will be apparent to those skilled in the art from this description taken in conjunction with the accompanying drawing which portrays diagrammatically one arrangement of equipment which has been found very suitable for carrying out the present invention in an embodiment thereof wherein benzene is alkylated.

General

In one aspect, the present invention involves a process for reacting a low-boiling aliphatic olefin, and especially the C₃ to C₆ olefins, namely, propylene, any of the three butylenes, and any of the pentenes, with an alkylatable cyclic organic compound, especially aromatic hydrocarbons and furan, to effect replacement of hydrogen atoms on the ring with alkyl groups corresponding to the olefin by intimately admixing the olefin-containing hydrocarbon material which almost invariably contains large proportions of the corresponding paraffin with liquid concentrated hydrofluoric acid in amount substantially equimolar to the olefin, maintaining the resulting mixture under conditions effecting substantially complete hydrofluorination of the olefin content as substantially the sole reaction, i. e., to the substantial exclusion of alkylation of any isoparaffin present in the feed, extracting the resulting mixture with sufficient added liquid concentrated hydrofluoric acid to form a separate liquid acid phase under conditions such that substantially complete extraction of the alkyl fluorides in said

liquid hydrofluoric acid phase is the principal result, separating the resulting extract from the raffinate which contains the paraffin and any small amount of alkylate formed by alkylation of a small amount of any isoparaffin present concomitantly with the extraction, directly admixing the extract with a molar excess of the alkylatable cyclic organic compound and subjecting the resulting mixture to conditions effecting alkylation of the cyclic organic compound with substantially all of the alkyl fluorides, and recovering the alkyl derivatives so produced as the product of the process.

In one specific embodiment, this invention is an improved process for reacting a low-boiling olefin and benzene to produce an alkylate in the presence of hydrofluoric acid, which comprises intimately admixing with a hydrocarbon material containing a low-boiling olefin hydrofluoric acid in a proportion substantially equimolecular to the olefin, maintaining the resulting mixture for not more than about 30 minutes, extracting said mixture with substantially anhydrous liquid hydrofluoric acid in an extraction step at an extraction temperature not greater than about 100° F., mixing with the resulting extract benzene in an alkylation zone under conditions such as to produce an alkylate, separating the effluent from said alkylation zone into a relatively light phase and a relatively heavy hydrofluoric acid phase, recovering said alkylate from said light phase, passing a major portion of said acid phase to said extraction step as a part of the extraction solvent, passing the raffinate from said extraction step to a distillation step for recovery of dissolved hydrofluoric acid therefrom, passing a minor portion of said acid phase to said distillation step for removal of organic impurities, and passing purified and recovered hydrofluoric acid from said distillation step to said extraction step.

Compounds alkylated

Any cyclic organic compound which is alkylatable with a low-boiling olefin in the presence of liquid substantially anhydrous hydrofluoric acid may be employed in carrying out the present invention. Ordinarily I alkylate either an aromatic hydrocarbon especially the normally monocyclic aromatics such as benzene, toluene, xylene, cumene, mesitylene, ethylbenzene, etc., or a so-called "superaromatic" such as furan. Instead of furan, its alkylatable homologs and derivatives may be used such as 2-furoic acid, methyl 2-furoate, 2-furyl-phenyl-ketone and the like. Furan is more easily alkylated than benzene and other alkylatable aromatics although it has a smaller number of replaceable hydrogen atoms per molecule. Similar alkylatable compounds, which in part may be characterized as having at least two conjugated double bonds in a ring, may be employed, examples being phenol, pyrrol, thiophene and homologs, but usually benzene and its homologs or furan is to be preferred.

Olefin-containing material

I may use any aliphatic olefin-containing material which contains any of the low-boiling olefins in admixture with a substantial proportion of diluent hydrocarbon so that separation by fractional distillation, azeotropic distillation, extractive distillation, solvent extraction or chemical methods must ordinarily be resorted to. My invention obviates such preliminary separation since the diluent which is generally low-boiling

paraffin, although hydrogen may also be present, is rejected as the raffinate in the extraction step which follows the hydrofluorination. Very often the diluent is the paraffin corresponding to the olefin. Hydrogen and methane have usually been removed by the usual means. The olefin is commonly a C₂ to C₅ olefin or mixture of such olefins. Since alkylation of isoparaffins with ethyl fluoride with anhydrous hydrogen fluoride as the catalyst is somewhat more difficult than in the case of propyl fluoride and the higher alkyl fluorides, the C₃ or higher olefins are often preferred. Since C₅ streams are often more valuable for other purposes, a C₃ and/or C₄ stream is more frequently employed in carrying out the present invention. A feed containing isobutylene and isobutene is very advantageously employed in the process of the present invention, the isobutylene giving valuable tertiary butyl derivatives and the isobutane being alkylated to only a limited extent in the hydrofluorination and alkylation steps of the invention and being rejected in the raffinate in the extraction step. The olefin-containing stream may be derived from any suitable source. Generally, it is prepared either by cracking or by dehydrogenation of a suitable feed stock such as crude oil, gas oil, naphtha, the corresponding paraffin, etc. It may be a by-product or the principal product of the cracking operation. Generally, undesired heavier and lighter materials are removed prior to the process of the present invention. For example, fixed gases such as hydrogen and methane are readily removed in the conventional manner and materials heavier than the desired olefin, such as tars, etc., are likewise easily removed. Preferably the olefin-containing feed is free from sulfur, oxygen and nitrogen compounds including mercaptan and hydrogen sulfide as well as elementary sulfur, since the presence of such compounds in the process ordinarily is undesirable.

The olefin-containing feed usually contains large proportions of the corresponding paraffin or paraffins. Generally, the feed will contain over 50% of paraffin and often more than 70% thereof ranging up to 90 or even 99%, the balance being olefin. It is a major advantage of the present invention that such dilute streams can be employed even in the case where an isoparaffin is present, since such isoparaffin is but little alkylated so that a maximum of the olefin is converted to the desired product, namely, the alkylated cyclic organic compound. Any isoparaffin that is alkylated is converted to highly branched higher isoparaffin especially where a branched olefin is employed, and such higher isoparaffin is readily recovered from the raffinate of the extraction step and forms a valuable by-product of the process.

Hydrofluorination step

In this step the olefin-containing feed is intimately admixed with substantially anhydrous liquid HF in an amount substantially stoichiometrically equal to the olefin and the mixture is subjected to reaction conditions effecting hydrofluorination of substantially all the olefin as substantially the sole reaction. The temperature may be in the range of 40 to 200° F. and preferably below 100° F. The pressure should be such as to maintain the hydrocarbons predominantly in liquid phase and may range from 100 to 300 pounds gage. The mol proportion of HF to olefin should preferably be within the range of from 1 to 1.1 times the total olefin. At proportions much above this range polymerization of

olefin and alkylation of isoparaffin, if present, may become considerable or excessive.

The resulting mixture is held under conditions favoring addition of hydrofluoric acid to the olefin without promoting polymerization of olefin or alkylation of any isoparaffin for a period of time sufficient to effect the desired hydrofluorination. This time may range from 2 up to 30 minutes. The conditions are those set forth in the preceding paragraph.

Extraction step

The reaction mixture leaving the hydrofluorination zone and consisting essentially of alkyl fluoride and the inerts, usually essentially paraffinic, is extracted with substantially anhydrous liquid hydrofluoric acid in amount sufficient to form a separate liquid phase sufficiently large to dissolve substantially all of the alkyl fluoride. The volume of hydrofluoric acid used should be equivalent in mols to about 5-20 or more times the number of mols of the alkyl fluorides present. Lesser proportions are likely to result in incomplete extraction of alkyl fluorides whereas greater proportions place an unnecessarily large quantity of hydrofluoric acid in circulation in the system and cause an excessive consumption of alkyl fluorides by alkylation of isoparaffin where present. The conditions of the extraction step are such that liquid-liquid extraction is accomplished, the hydrocarbon phase and the hydrofluoric acid phase being intimately mixed or emulsified with one another followed by a separation of the raffinate phase containing the inert components including any isoparaffin and the extract phase in a conventional manner. The time of contacting may range from 30 seconds to 5 minutes. The shorter the contacting the better is the result as long as intimate contacting of acid and hydrocarbon is attained. When the time is excessively long decomposition and degradation of the alkyl fluorides and alkylation of any isoparaffin take place to an objectionable extent. The temperature should be as low as economically feasible within the range of -20 to 100°F . in order to minimize solution of hydrofluoric acid in the hydrocarbon phase. The contacting may be accomplished in the conventional contactor or mixing pump followed by the usual gravitational layering and separation equipment which is likewise maintained at a temperature not over 100°F ., the separation of layers likewise being carried out as rapidly as possible in order to minimize objectionable side reactions.

I have found that the extraction may be very satisfactorily conducted with the amount of separate liquid hydrofluoric acid phase ranging from approximately 0.2 to 0.3 times the volume of the hydrocarbon phase. By limiting the amount of separate liquid hydrofluoric acid phase in the extraction step, alkylation of the isoparaffin derived from the olefin containing feed is kept at a desirable minimum.

The raffinate from the extraction step is ordinarily passed to a fractionation step wherein the hydrofluoric acid contained therein is recovered as an overhead for recycle to the extraction step from a bottoms product containing inert material. Where isoparaffin is present in the feed and alkylation thereof to any substantial extent takes place in the hydrofluorination and/or extraction step, the resulting higher isoparaffin may be recovered by fractional distillation of the raffinate.

Alkylation step

The extract from the extraction step is passed to an alkylation zone to which is also supplied the cyclic organic compound which is to be alkylated in accordance with the present invention. The reaction conditions in the alkylation zone are well known to those skilled in the art of hydrofluoric acid alkylation and may comprise a temperature in the range of -20 to 200°F ., sufficient pressure to maintain liquid phase, an average reaction time in the range of from 1 to 100 minutes, good agitation, a mol ratio of cyclic organic compound to alkyl fluoride of from 1.5 to 10 or more, a ratio of from 5 to 10 being preferred, and a hydrocarbon-to-catalyst volume ratio in the range of from 0.2 to 4. Ordinarily the conditions of the alkylation are so adjusted that the mono-alkyl derivatives of the cyclic organic compound is the predominant or nearly the entire (say at least 90%) alkylated product of the alkylation reaction, since generally the polyalkyl derivatives are not as desirable as the mono-alkyl compounds. Any of the usual contacting devices commonly employed in alkylation may be employed. The alkylation effluent is allowed to separate by gravity or other means into two liquid phases, namely, a lighter organic phase containing the desired alkylated organic compound and a heavier acid phase. The organic phase is treated in any suitable manner usually by fractionation to recover the alkylated organic compound as the product of the process. Any hydrofluoric acid dissolved therein may also be recovered or recycled to the extraction step. The acid phase is preferably in part recycled to the extraction step and in part passed to the same fractionation column wherein the raffinate described above is distilled. In this way the hydrogen fluoride is recovered as an overhead for recycle to the extraction step from a bottoms product containing in addition to the inert compounds derived from the raffinate the acid-soluble oils contained in the acid phase.

Drawing

Referring to the accompanying drawing the olefin containing feed and substantially pure hydrofluoric acid are fed via lines 1 and 2, respectively, to mixer 3. The mixture is held in time tank 4 for the necessary period of time to accomplish hydrofluorination of olefin. The resulting mixture is then passed into extractor 5 where it is liquid-liquid extracted with liquid hydrofluoric acid introduced by line 6. The raffinate passes via lines 7 and 8 to column 9 or, where isoparaffin alkylation takes place to limited extent, via line 10 into the column 11 which separates it into an overhead of hydrofluoric acid and isobutane which may be recycled via lines 12 and 13 and a bottoms product containing the isoparaffin alkylate withdrawn via line 14.

The extract separated in extractor 5 is passed via line 15, with added HF introduced via line 16 if desired, to alkylator 17 where the alkylation takes place. Benzene or other cyclic organic compound to be alkylated is introduced to alkylator 17 via line 18 which may enter unit 17 at any suitable point therein. The alkylation effluent is fed into separator 19 where phase separation takes place. The organic phase is passed via line 20 to fractionation unit 21 wherein is separated, for example, a benzene recycle which is returned via line 22 to the alkylation zone, a fraction of unreacted HF which is recycled to the extraction

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step via lines 23 and 13 and a fraction of alkylated benzene or other cyclic organic compound withdrawn as bottoms product via line 24.

The acid phase separated in unit 19 is withdrawn via line 25 and conventionally separated into two streams, one stream being recycled to extraction unit 5 via line 26 and the second, which should be sufficiently large to keep the hydrofluoric acid in the system at the desired level of purity, is passed via line 27 into column 9 wherein it is distilled together with the raffinate feed thereto via line 8. In this way the hydrogen fluoride contained in this portion of the acid phase is recovered in purified form from the acid-soluble oils which are recovered in admixture with the inert components of the raffinate via line 28.

Example I

To a refinery fraction comprising about 10 mol per cent propylene and 90 mol per cent propane is added in a centrifugal-type mixer a proportion of concentrated hydrofluoric acid molecularly equivalent to the propylene. The mixture passes to a reaction vessel maintained at a temperature below about 80 to 90° F. by cold water coils. The residence time in this vessel is about 10 to 20 minutes. The vessel is provided with a stirrer to prevent the separation of a hydrofluoric acid layer in the bottom. From this vessel the mixture passes to another centrifugal-type mixer into which is introduced an additional quantity of concentrated hydrofluoric acid approximately equal in volume to the total original propylene-containing stream. The resulting mixture passes to a centrifugal separator, from which the heavier or hydrofluoric acid phase is withdrawn and passes immediately to an alkylating zone. Into the alkylating zone is introduced benzene in a mol proportion about 5 to 10 times that of the original propylene. The alkylation temperature is about 80 to 120° F.; the pressure, about 50 to 150 p. s. i.; and the reaction time, about 5 to 30 minutes. The effluent mixture from the alkylating zone is separated into an acid layer which is recycled to the two mixers mentioned hereinbefore, and a hydrocarbon phase which is further separated by fractional distillation into hydrofluoric acid and unreacted-benzene recycle fractions and into an alkylate product fraction. The exact nature of the product depends somewhat on the alkylation conditions, as is indicated by the following illustrative data:

Run	A	B
Temperature, °F.	118	118
Pressure, p. s. i.	51	51
Contact time, min.	20.3	30.9
Benzene/propylene, mol.	8.3	5.4
Hydrocarbon/HF, vol.	1.3	1.4
Benzene-free alkylate:		
Yield, Wt. per cent of olefin	249	229
Olefin content, Wt. per cent	0.0	0.0
Organic fluorine, Wt. per cent	0.0005	0.0004
Composition, vol. per cent—		
Isopropylbenzene	93.5	91.0
Diisopropylbenzene	5.5	8.0
Heavier	1.0	1.0

Example II

Isobutane is catalytically dehydrogenated to the extent of about 20 to 30 per cent, as by a catalyst comprising chromium oxide under suitable dehydrogenation conditions, in a manner well-known to the art. The resulting effluent is cooled and is substantially freed from light gases. To it in liquefied condition is added hydrofluoric

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acid in a proportion approximately molecularly equivalent to the butylene content. After a reaction period of about 10 to 15 minutes, the resulting mixture is rapidly countercurrently extracted with approximately 0.2 to 0.3 times its own volume of additional liquid hydrofluoric acid, or, generally, with the minimal volume sufficient to remove substantially all of the tertiary butyl fluoride from the mixture, whereby concomitant alkylation of isobutane is minimized. The extract is passed immediately to an alkylation zone at approximately the alkylation conditions cited in Example I, wherein it is intimately agitated with a several-fold molecular excess of benzene; additional hydrofluoric acid is added, to increase the acid-to-hydrocarbon ratio to approximately 1:1 by volume. The resulting mixture is then separated into two liquid layers, and the lower layer is recycled and/or purified. The upper layer is freed from acid and is then fractionally distilled to isolate the alkylate product boiling above benzene. Illustrative data for this product are:

Yield, Wt. per cent of olefin	200
Olefin content, Wt. per cent	0.0
Organic fluorine, Wt. per cent	0.0003
Composition, vol. per cent:	
Tert-butylbenzene	92.0
Di-tert-butylbenzene	7.5
Heavier	0.5

The foregoing description is to be taken as illustrative only and not as limiting the invention which is to be interpreted as limited solely by the language of the appended claims.

I claim:

1. An improved process for reacting a low-boiling olefin and an alkylatable cyclic organic compound to produce alkyl derivatives of said cyclic organic compound by replacement of hydrogen atoms on the ring with alkyl groups corresponding to said olefin in the presence of a hydrofluoric acid catalyst, which comprises intimately admixing a hydrocarbon material containing a low-boiling olefin with liquid hydrofluoric acid in an amount substantially equimolar to said olefin, maintaining said admixture for not more than about 30 minutes, intimately admixing with the resulting material a substantial excess of liquid concentrated hydrofluoric acid as an extraction liquid in an extraction step at an extraction temperature not greater than about 100° F. and subsequently separating a hydrocarbon phase and a first liquid hydrofluoric acid phase, intimately admixing an alkylatable cyclic organic compound with said liquid hydrofluoric acid extract phase under reaction conditions such as to effect alkylation of said cyclic organic compound to produce said alkyl derivatives thereof, separating effluents of said reaction into an organic phase and a second liquid hydrofluoric acid phase, recovering said alkyl derivatives of said cyclic organic compound from said organic phase, passing a major portion of said second acid phase to said extraction step as a part of said extraction liquid, passing said hydrocarbon phase to a distillation step for recovery of dissolved hydrogen fluoride therefrom, passing a minor portion of said second acid phase to said distillation step for removal of organic impurities, and recovering from said distillation step purified hydrogen fluoride and passing same to said extraction step.

2. An improved process for reacting a low-boiling olefin and an alkylatable aromatic hydrocarbon to produce alkyl derivatives of said aromatic hydrocarbon by replacement of hydrogen

atoms on the ring with alkyl groups corresponding to said olefin in the presence of a hydrofluoric acid catalyst, which comprises intimately admixing a hydrocarbon material containing a low-boiling olefin with liquid hydrofluoric acid in an amount substantially equimolar to said olefin, maintaining said admixture for not more than about 30 minutes, intimately admixing with the resulting material a substantial excess of liquid concentrated hydrofluoric acid as an extraction liquid in an extraction step at an extraction temperature not greater than about 100° F. and subsequently separating a first hydrocarbon phase and a first liquid hydrofluoric acid phase, intimately admixing aromatic hydrocarbon with said liquid hydrofluoric acid phase under reaction conditions such as to effect alkylation of said aromatic hydrocarbon to produce said alkyl derivatives thereof, separating effluents of said reaction into a second hydrocarbon phase and a second liquid hydrofluoric acid phase, recovering said alkyl derivatives of said aromatic hydrocarbon from said second hydrocarbon phase, passing a major portion of said second acid phase to said extraction step as a part of said extraction liquid, passing said first hydrocarbon phase to a distillation step for recovery of dissolved hydrogen fluoride therefrom, passing a minor portion of said second acid phase to said distillation step for removal of organic impurities, and recovering from said distillation step purified hydrogen fluoride and passing same to said extraction step.

3. An improved process for reacting a low-boiling olefin and benzene to produce alkyl derivatives of benzene by replacement of hydrogen atoms on the ring with alkyl groups corresponding to said olefin in the presence of a hydrofluoric acid catalyst, which comprises intimately admixing a hydrocarbon material containing a low-boiling olefin with liquid hydrofluoric acid in an amount substantially equimolar to said olefin, maintaining said admixture for not more than about 30 minutes, intimately admixing with the resulting material a substantial excess of liquid concentrated hydrofluoric acid as an extraction liquid in an extraction step at an extraction temperature not greater than about 100° F. and subsequently separating a first hydrocarbon phase and a first liquid hydrofluoric acid phase, intimately admixing benzene with said liquid hydrofluoric acid phase under reaction conditions such as to effect alkylation of said benzene to produce said alkyl derivatives thereof, separating effluents of said reaction into a second hydrocarbon phase and a second liquid hydrofluoric acid phase, recovering said alkyl derivatives of said benzene from said second hydrocarbon phase, passing a major portion of said second acid phase to said extraction step as a part of said extraction liquid, passing said first hydrocarbon phase to a distillation step for recovery of dissolved hydrogen fluoride therefrom, passing a minor portion of said second acid phase to said distillation step for removal of organic impurities, and recovering from said distillation step purified hydrogen fluoride and passing same to said extraction step.

4. An improved process for reacting a low-boiling olefin and furan to produce alkyl derivatives of furan by replacement of hydrogen atoms on the ring with alkyl groups corresponding to said olefin in the presence of a hydrofluoric acid catalyst, which comprises intimately admixing a hydrocarbon material containing a low-boiling olefin with liquid hydrofluoric acid in an amount

substantially equimolar to said olefin, maintaining said admixture for not more than about 30 minutes, intimately admixing with the resulting material a substantial excess of liquid concentrated hydrofluoric acid as an extraction liquid in an extraction step at an extraction temperature not greater than about 100° F. and subsequently separating a hydrocarbon phase and a first liquid hydrofluoric acid phase, intimately admixing furan with said liquid hydrofluoric acid phase under reaction conditions such as to effect alkylation of said furan to produce said alkyl derivatives thereof, separating effluents of said reaction into an organic phase and a second liquid hydrofluoric acid phase, recovering said alkyl derivatives of said furan from said organic phase, passing a major portion of said second acid phase to said extraction step as a part of said extraction liquid, passing said hydrocarbon phase to a distillation step for recovery of dissolved hydrogen fluoride therefrom, passing a minor portion of said second acid phase to said distillation step for removal of organic impurities, and recovering from said distillation step purified hydrogen fluoride and passing same to said extraction step.

5. An improved process for reacting propylene with an alkylatable cyclic organic compound to produce propyl derivatives of said cyclic organic compound by replacement of hydrogen atoms on the ring with propyl groups which comprises intimately admixing a normally gaseous hydrocarbon material containing propylene and propane with liquid hydrofluoric acid in an amount substantially equimolar to said propylene, maintaining said admixture for not more than about 30 minutes, intimately admixing with the resulting material a substantial excess of liquid concentrated hydrofluoric acid as an extraction liquid in an extraction step at an extraction temperature not greater than about 100° F. and subsequently separating a hydrocarbon phase and a first liquid hydrofluoric acid phase, intimately admixing an alkylatable cyclic organic compound with said liquid hydrofluoric acid phase under reaction conditions such as to effect alkylation of said cyclic organic compound to produce said propyl derivatives thereof, separating effluents of said reaction into an organic phase and a second liquid hydrofluoric acid phase, recovering said propyl derivatives of said cyclic organic compound from said organic phase, passing a major portion of said second acid phase to said extraction step as a part of said extraction liquid, passing said hydrocarbon phase to a distillation step for recovery of dissolved hydrogen fluoride therefrom, passing a minor portion of said second acid phase to said distillation step for removal of organic impurities, and recovering from said distillation step purified hydrogen fluoride and passing same to said extraction step.

6. An improved process for reacting propylene with benzene to produce propyl derivatives of said benzene by replacement of hydrogen atoms on the ring with propyl groups which comprises intimately admixing a normally gaseous hydrocarbon material containing propylene and propane with liquid hydrofluoric acid in an amount substantially equimolar to said propylene, maintaining said admixture for not more than about 30 minutes, intimately admixing with the resulting material a substantial excess of liquid concentrated hydrofluoric acid as an extraction liquid in an extraction step at an extraction temperature not greater than about 100° F. and subsequently separating

rating a first hydrocarbon phase and a first liquid hydrofluoric acid phase, intimately admixing benzene with said liquid hydrofluoric acid phase under reaction conditions such as to effect alkylation of said benzene to produce said propyl derivatives thereof, separating effluents of said reaction into a second hydrocarbon phase and a second liquid hydrofluoric acid phase, recovering said propyl derivatives of said benzene from said second hydrocarbon phase, passing a major portion of said second acid phase to said extraction step as a part of said extraction liquid, passing said first hydrocarbon phase to a distillation step for recovery of dissolved hydrogen fluoride therefrom, passing a minor portion of said second acid phase to said distillation step for removal of organic impurities, and recovering from said distillation step purified hydrogen fluoride and passing same to said extraction step.

7. An improved process for reacting propylene with furan to produce propyl derivatives of said furan by replacement of hydrogen atoms on the ring with propyl groups which comprises intimately admixing a normally gaseous hydrocarbon material containing propylene and propane with liquid hydrofluoric acid in an amount substantially equimolar to said propylene, maintaining said admixture for not more than about 30 minutes, intimately admixing with the resulting material a substantial excess of liquid concentrated hydrofluoric acid as an extraction liquid in an extraction step at an extraction temperature not greater than about 100° F. and subsequently separating a hydrocarbon phase and a first liquid hydrofluoric acid phase, intimately admixing furan with said liquid hydrofluoric acid phase under reaction conditions such as to effect alkylation of said furan to produce said propyl derivatives thereof, separating effluents of said reaction into an organic phase and a second liquid hydrofluoric acid phase, recovering said propyl derivatives of said furan from said organic phase, passing a major portion of said second acid phase to said extraction step as a part of said extraction liquid, passing said hydrocarbon phase to a distillation step for recovery of dissolved hydrogen fluoride therefrom, passing a minor portion of said second acid phase to said distillation step for removal of organic impurities, and recovering from said distillation step purified hydrogen fluoride and passing same to said extraction step.

8. An improved process for reacting isobutylene and an alkylatable cyclic organic compound to produce tertiary butyl derivatives of said cyclic organic compound by replacement of hydrogen atoms on the ring with tertiary butyl groups in the presence of a hydrofluoric acid catalyst, which comprises intimately admixing a normally gaseous hydrocarbon containing isobutylene and isobutane in liquid phase with liquid hydrofluoric acid in an amount substantially equal to the butylene content of said hydrocarbon, maintaining said admixture for not more than about 30 minutes, intimately admixing with the resulting material a substantial excess of liquid concentrated hydrofluoric acid as an extraction liquid in an extraction step at an extraction temperature not greater than about 100° F., subsequently separating a hydrocarbon phase and a first hydrofluoric acid phase, intimately admixing an alkylatable cyclic organic compound with said liquid hydrofluoric acid phase under reaction conditions such as to effect alkylation of said cyclic organic compound to produce tertiary butyl derivatives thereof, separating effluents of said

reaction into an organic phase and a second liquid hydrofluoric acid phase, and recovering said tertiary butyl derivatives of said cyclic organic compound from said organic phase.

9. An improved process for reacting isobutylene and benzene to produce tertiary butyl derivatives of benzene by replacement of hydrogen atoms on the ring with tertiary butyl groups in the presence of a hydrofluoric acid catalyst, which comprises intimately admixing a normally gaseous hydrocarbon containing isobutylene and isobutane in liquid phase with liquid hydrofluoric acid in an amount substantially equal to the butylene content of said hydrocarbon, maintaining said admixture for not more than about 30 minutes, intimately admixing with the resulting material a substantial excess of liquid concentrated hydrofluoric acid as an extraction liquid in an extraction step at an extraction temperature not greater than about 100° F., subsequently separating a first hydrocarbon phase and a first liquid hydrofluoric acid phase, intimately admixing benzene with said first liquid hydrofluoric acid phase under reaction conditions such as to effect alkylation of benzene to produce tertiary butyl derivatives thereof, separating effluents of said reaction into a second hydrocarbon phase and a second liquid hydrofluoric acid phase, and recovering said tertiary butyl derivatives of benzene from said second hydrocarbon phase.

10. An improved process for reacting isobutylene and furan to produce tertiary butyl derivatives of furan by replacement of hydrogen atoms on the ring with tertiary butyl groups in the presence of a hydrofluoric acid catalyst, which comprises intimately admixing a normally gaseous hydrocarbon containing isobutylene and isobutane in liquid phase with liquid hydrofluoric acid in an amount substantially equal to the butylene content of said hydrocarbon, maintaining said admixture for not more than about 30 minutes, intimately admixing with the resulting material a substantial excess of liquid concentrated hydrofluoric acid as an extraction liquid in an extraction step at an extraction temperature not greater than about 100° F., subsequently separating a hydrocarbon phase and a first hydrofluoric acid phase, intimately admixing furan with said liquid hydrofluoric acid phase under reaction conditions such as to effect alkylation of furan to produce tertiary butyl derivatives thereof, separating effluents of said reaction into an organic phase and a second liquid hydrofluoric acid phase, and recovering said tertiary butyl derivatives of furan from said organic phase.

11. The process of claim 8 wherein higher isoparaffin formed in said extraction step by alkylation of isobutane and appearing in said hydrocarbon phase is separately recovered by passing said hydrocarbon phase to a distillation zone and there separating said higher isoparaffin from the isobutane and hydrogen fluoride, and wherein said isobutane and hydrogen fluoride so recovered are recycled to said extraction step.

12. A process for reacting a low-boiling aliphatic olefin and an alkylatable cyclic organic compound to produce alkyl derivatives of said cyclic organic compound by replacement of hydrogen atoms on the ring with alkyl groups corresponding to said olefin which comprises intimately admixing a hydrocarbon material containing said olefin and the corresponding paraffin with liquid hydrofluoric acid in amount substantially equimolar to said olefin, maintaining the resulting mixture under conditions effecting substan-

tially complete hydrofluorination of said olefins as substantially the sole reaction, extracting the resulting mixture with sufficient liquid hydrofluoric acid to form a separate liquid phase under conditions such that substantially complete extraction of the alkyl fluorides in said liquid hydrofluoric acid phase is the principal result, separating the resulting extract from the resulting raffinate, directly admixing said extract with a molar excess of said alkylatable cyclic organic compound and subjecting the mixture to conditions effecting alkylation of said cyclic organic compound with substantially all of said alkyl fluorides, and recovering said alkyl derivatives of said cyclic organic compound from the alkylation effluent.

13. The process of claim 12 wherein said cyclic organic compound is introduced to said alkylation step in a mol proportion of from 5 to 10 times that of the alkyl fluoride present.

14. The process of claim 12 wherein said corresponding paraffin is an isoparaffin, wherein substantial alkylation thereof in said hydrofluorination step is avoided, and wherein alkylation thereof in said extraction step is minimized.

15. The process of claim 8 wherein said extraction step is conducted as a liquid-liquid extraction at a temperature not greater than about 100° F. and with the amount of separate liquid hydrofluoric acid phase ranging from approximately 0.2 to 0.3 times the volume of the hydrocarbon phase.

16. The process of claim 12 wherein said extraction step is conducted as a liquid-liquid extraction at a temperature not greater than about 100° F. and with the amount of separate liquid hydrofluoric acid phase ranging from approximately 0.2 to 0.3 times the volume of the hydrocarbon phase.

17. The process which comprises alkylating furan with a lower alkyl fluoride in the presence of liquid substantially anhydrous hydrofluoric acid as the catalyst.

18. The process which comprises alkylating an alkylatable organic compound having a five-membered heterocyclic ring with an alkyl fluoride in the presence of liquid hydrofluoric acid as a catalyst.

19. A process which comprises alkylating an alkylatable thiophene with an alkyl fluoride using liquid hydrofluoric acid as a catalyst.

20. The process which comprises alkylating an alkylatable furan with an alkyl fluoride in the presence of hydrofluoric acid as a catalyst.

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REFERENCES CITED

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

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Number	Name	Date
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