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3,272,879

HIGH ENERGY FUELS AND METHODS

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3 Claims. (Cl. 260—668)

This application is a continuation-in-part of application Serial No. 833,996 filed August 17, 1959, now Patent No. 3,105,351.

This invention relates to mixtures comprising position isomers of bridged saturated hydrocarbons having various uses, but particularly as a high energy fuel for jet, turbojet, rocket, missile and other reaction engines; to intermediate mixtures of position isomers of bridged unsaturated polycyclic hydrocarbons useful to form said saturated polycyclic hydrocarbons by hydrogenation, and having other uses; and to alkylating processes for forming said intermediate mixtures by alkylating monocarbocyclic aryl or an alkyl monocarbocyclic compound with carbocyclic alkene compound.

Other secondary uses of my mixture of bridged saturated and unsaturated compounds include heat transfer fluids, hydraulic fluids and transformer oils. They are also useful as high stability lubricants, plasticizers, extenders and softeners of elastic and plastic materials. It will be apparent moreover, that several such uses may be exploited for a single composition; for instance, the product may first be used in lubrication and/or in heat exchange, and/or as a hydraulic transfer fluid before being consumed as a jet fuel.

In my prior copending application Serial Number 833,996, filed August 17, 1959, now Patent No. 3,105,351 of which the present application is a continuation-in-part, I described and claimed alkyl dicyclohexyl alkane, compounds having the above named uses, particularly as jet fuels because of their high gravity and high B.t.u. values. Moreover a preference for compounds having from 14 to 30 carbon atoms was indicated because these are usually liquid at ambient temperatures. Such compounds were described to be formed by full hydrogenation of compounds resulting from the bridging of two benzene rings to an acetylene, or aldehyde or other difunctional bridging group, the mixture reacting first to form a mono alkyl benzene intermediate, which then further condenses with a second alkyl benzene ring compound to effect a bridging of usually two alkyl benzene rings and thus form a di(alkyl phenyl)-alkane. However, such intermediates can also form higher solid polycyclic alkane bridged compounds tending to decrease the yield of desirable liquid dicyclic alkane bridged compounds.

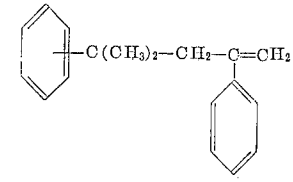
I have now found that the formation of the higher polycyclopolyalkane side reaction products are reduced to form better jet fuel or products for the other uses listed, using a more economical reaction with more economically available starting materials by starting with an intermediate ring compound either aromatic preferably monocarbocyclic, or cycloalkyl of 5 or 6 carbon atoms, which carry an alkenyl side chain, preferably having at least one double bond alpha-beta with respect to the ring, and which may be designated by the following formula:

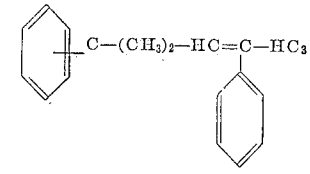
FORMULA I

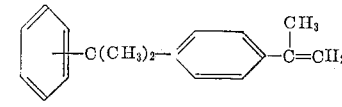
$$(R'')_{p-1}—Ar(—\underset{R}{C}=\underset{R'}{C}H)_n$$

wherein R and R' are hydrogen, straight or branched chain alkyl, Ar-alkyl, alkenyl, or Ar-alkenyl which, together with the ethylene group, comprise a side chain of up to 12 carbon atoms, R'' is hydrogen, or straight or branched chain alkyl, Ar-alkyl, or Ar-alkenyl, of up to

12 carbon atoms in which R, R', and R'' can be the same or different, Ar is benzene or 5 or 6 carbon atom cycloalkane, n is an integer of from 1 to 3 and p is an integer of from 1 to 5. Typical alpha-beta unsaturated side chain intermediates of Formula I are styrene, alpha-methyl styrene, alpha-ethyl styrene, vinyl toluenes, vinyl-ethyl benzenes, propenyl benzene, butenyl benzene, isobutenyl benzene, butadienyl benzene, piperylenyl benzene, heptenyl benzene, decenyl benzene, o-phenyl butenyl vinyl-benzene, divinyl benzenes, butenyl styrenes, tri-vinyl benzenes, alpha-methyl vinyl toluene, alpha-methyl vinyl xylenes, alpha-ethyl vinyl toluenes, hexyl vinyl benzenes, vinyl xylenes, trimethyl styrenes, vinyl-ethyl methyl benzenes, vinyl tertiary butyl benzenes, vinyl cyclohexane, alpha-methyl vinylcyclohexane vinyl cyclopentane, divinyl cyclohexanes, undecenyl styrenes, dodecenyl styrenes, alpha-decylstyrene, 2,4-diphenyl-4-methyl pentene-1, 2,4-diphenyl-4-methyl pentene-2, 4-(2-phenyl isopropyl)-alpha-methylstyrene (the last three being dimer forms of alpha methyl styrene) and respectively corresponding to the structural formulae:



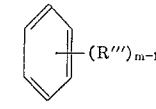




1,3-diphenyl butene-2, 1,3-diphenyl butene-1, 2-(2-phenyl ethyl)styrene (the last two being dimers of styrene) and the like such as dimers of the vinyl toluenes, vinyl xylenes, alpha-ethyl styrenes, and other vinyl aromatic compounds listed and the like, as well as commercial mixtures thereof.

The intermediate compound of Formula I is reacted by alkylation of the ring with an alkyl benzene compound of the formula:

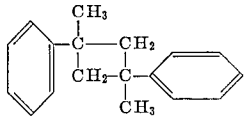
FORMULA II



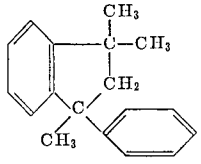
Where R''' is the same or different straight or branched chain alkyl, Ar-cycloalkyl, indanyl and alkindanyl having from 1 to 12 carbon atoms, Ar being the same as defined under Formula I, and m is an integer of 1 to 5, preferably 2 to 4.

Typical starting material compounds of Formula II are benzene, toluene, o-, m-, p-, xylenes, ethyl benzene, mesitylene, cumene, diethyl benzenes, methylethyl benzenes, dimethyl ethyl benzenes, tetramethyl benzenes, amyl benzene, diisooctyl benzenes, dipropyl benzenes, dodecylbenzene, triisopropyl benzene, diisobutyl benzenes, di-2-ethyl hexyl benzene, dicyclohexyl benzenes, cyclohexyl methyl benzene, 2,2,4-trimethyl pentyl benzene, ditertiary butyl benzenes, 1,3-dimethyl-1,3-diphenyl cyclobutane, 1,3-diphenyl cyclobutane, (the last two dimers of a alpha-

methyl styrene and styrene respectively) of which the alpha methyl styrene dimer has the structure



1,3,3-trimethyl-1-phenyl indan (another dimer of alpha methyl styrene having the structure:



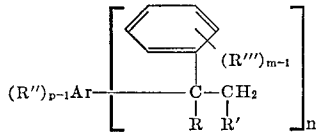
1,3,3,5,6 - pentamethyl - 1(3,4 - dimethyl phenyl) indane (a dimer of vinyl xylene) and similar saturated ring-benzene derivatives and the like.

A preferred starting material is a C_6–C_9 aromatic fraction obtained as an aromatic petroleum extract; and sometimes obtained as a mixture with compounds of Formula I such as with about 15 to 80% of styrene formed by dehydrogenation of ethyl benzene or ethyl benzene containing fractions, the product being predominantly unreacted benzene, styrene formed therefrom and relatively minor quantities of other aromatics formed in the decomposition, such as the xylenes, toluene and small quantities of benzene.

During the alkylation reaction as described below, some of the compounds of Formula I can dimerize. These often produce compounds of two types, one type having a residual unsaturated side chain and are included in the definition of Formula I, and the other type being saturated, are included in the definition of Formula II. To the extent they are produced in an alkylated material the dimers can be ultimately, but not necessarily be removed if desired. They can be removed from the alkylate by a combination of distillation and crystallization.

In the broadest aspect of this invention, a compound of Formula I is reacted to alkylate a compound of Formula II to form, predominantly a compound of the following structural Formula III:

FORMULA III

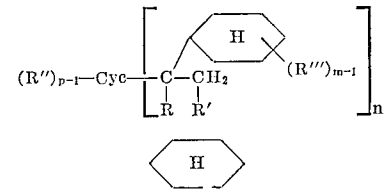


in which R, R', R'', R''', Ar, *m*, *n* and *p* have the same definition as given for Formulae I and II. In this reaction a free nuclear carbon atom of the aromatic ring of Formula II attached to the alpha carbon atom of the olefinic side chain of Formula I.

For production of a jet fuel and often for the other uses, the entire reaction product is exhaustively hydrogenated to saturate all side chains and rings. That hydrogenation can be drastic, as disclosed in my aforesaid patent application, S.N. 833,996, now Patent No. 3,105,351, at pressures usually in the range of 500 to 5000 p.s.i. and at temperatures, not critical, but usually in the range of 100 to 200° C. in the presence of a hydrogenation catalyst such as nickel, cobalt or other catalyst useful for hydrogenating the aromatic ring, for example, Raney nickel or Raney cobalt. However, it is sometimes preferred to hydrogenate mildly at first merely to saturate excessive side chain unsaturation, to temperatures below about 90° C. and pressures below 250 p.s.i. and then to hydrogenate more drastically as described below to saturate the aromatic rings, for improved process flexibility and control of the character of the intermediates.

The structure of the final hydrogenation products may be generally illustrated by the following formula:

FORMULA IV



is a cyclohexane ring and wherein R and R' are hydrogen, alkyl and Cyc-alkyl, R and R'', straight or branched chain, together with the ethyl group having from 2 to 12 carbon atoms, R'' hydrogen, straight and branched chain alkyl and Cyc alkyl, R''' is alkyl, Cyc-cyclo alkyl, hexadroindanyl and hexahydroalkindanyl having from 1 to 12 carbon atoms, Cyc being the hydrogenation product of Ar; *m*, *n*, and *p* are the same as defined above for Formulae I and II.

In a more specific aspect, it will be noted, comparing compounds of Formula IV to compounds of applicants parent case, the variation of isomers with respect to the several ring substituent positions is fixed as to the Formula I portion of the final product, but may be varied for many available positions of the Formula II portion. That results in reducing the number of position isomers available in the Formula III product. However, it will be noted that the reaction product comprises the addition of an aromatic ring carbon atom to the alpha carbon atom of the olefinic chain, and a hydrogen atom from the said aromatic ring adds to the beta carbon of the olefinic linkage. This unsaturated linkage of the olefinic chain is saturated thereby. An immediate effect is the production of a dicyclic methylene or alkylidene derivative. These compounds are inherently more stable than compounds in which the cyclic radicals are separated by long alkylene bridging groups. Moreover, where the olefinic chain of the formula already carries an alpha hydrocarbon substituent, that is, where R in Formula I is hydrocarbon, for example, the compound produced (Formula III) is a tetrahydrocarbon substituted methane of which two of the substitutents are cyclic and two others are aliphatic hydrocarbon, whereby a compound which is outstandingly stable is produced.

Most important in this aspect of the invention is that the reaction components of both Formula I and Formula II are most readily available commercially from sources of great economy. For instance, in the commercial production of a simple olefin-substituted aromatic of Formula I such as styrene, ethyl benzene is dehydrogenated by passing under a drastic temperature and pressure conditions over a catalyst to form variable quantities of styrene which can be adjusted in the range of 15 to 85% styrene, together with several residual components in the mixture produced, components which may be regarded as typical Formula II compounds; that is, they are predominantly unreacted ethyl benzene and some toluene and traces of benzene. Pure styrene can be separated from this reaction mixture and an adjusted proportion of the residual mixture used herein.

Total reaction mixture product, however, according to a preferred practice of this invention is directly useful herein as a reaction mixture for forming the compounds of Formula III, which can then be hydrogenated. When the styrene manufacturing process is performed only to make feed for the present invention, it is sometimes preferred to operate the ethylbenzene dehydrogenation process at higher feed rates than usual for making pure styrene, that is, to produce product effluents containing from 20 to 30% styrene so that the hydrocarbon of Formula II constitutes from 70 to 80% of the products.

Another typical reaction mixture which is useful herein is the dehydrogenation product of cumene which con-

tains as a reaction mixture substantial quantities of alpha methyl styrene and includes in the reaction mixture unreacted cumene so that mixture may be directly alkylated for production, after the final hydrogenation, of a most stable jet fuel product.

Another important factor is that in the production of styrene most expensive preconditioning to produce a purified ethyl benzene is carried out. For present purposes, however, ethyl benzene even as occurring in a crude C_8 hydrocarbon fraction containing large amounts of other aromatics or higher components such as cumene need not be separated from the ethyl benzene but which entire crude aromatic mixture may be dehydrogenated to produce a mixture suitable for reaction to form compounds of Formula III.

Thus, while fewer position isomers are formed by the present reaction as compared to those of my parent application, a greater number of homologues may be present variable as to the type of alkyl in the structural product selected as desired. These may be allowed to remain and be used as a final jet fuel for greater economy or may be separated from the mixture by final selected distillation.

My compounds of Formula III according to the present invention are made by reacting Formula II compounds with Formula I compounds in the presence of Lewis acids or Friedel-Crafts type catalyst. In the reaction with Lewis acids or with the Friedel-Crafts type catalyst, the reaction is generally run at moderate, sometimes ambient temperatures, usually not exceeding 90° C. as an upper limit to substantially low temperatures, usually above about minus 70° C. The reaction in any case is exothermic and even when run at high ambient such as 25 to 70° C. temperatures, provisions are also made to reduce excessive heat development. Hence the reaction system used would normally include cooling means. By Lewis acids are meant substances having the ability to accept electrons (a more conventional definition of acids is "substances having a tendency to lose a proton"). Thus Lewis acids include any substance in non-aqueous systems as well as in aqueous systems, which readily accepts a pair of electrons and thus includes Friedel-Crafts catalysts conforming to HMeXn where Me is a metal of $n-1$ valence, X=halogen and n=an integer from 2 to 6, the $(MeX_n)^-$ ion being readily formed therefrom, e.g., BF_4^-, $AlCl_4^-$, $FeCl_4^-$, $SnCl_5^-$, $SbCl_6^-$, and the like. Lewis acids also include HF, H_2SO_4, BF_3—H_3PO_4, P_2O_5—H_2SO_4, H_3PO_4, $H_4P_2O_7$, and the like which may be used in both aqueous and anhydrous catalyst systems of this invention. Friedel-Crafts catalysts are often used with promoters, e.g., aluminum chloride is often used in admixture with promoters such as nitromethane, nitrobenzene, carbon tetrachloride, alkyl halide, alcohols, water, hydrogen chloride and the like.

The reaction may be run in three different ways to obtain distinctly modified products in each. It will be apparent that in the process wherein a Lewis acid catalyst of the type described herein is employed, direct addition of such catalyst to the Formula I component would result in immediate polymerization thereof. This may be controlled by my procedures so that either low amounts or large amounts of dimer may be obtained as desired. Some of the dimerized products are present in even the preferred most efficient alkylation method A. The quantity of dimer appearing either as Formula I or Formula II compounds is readily controlled by these methods.

A. ALKYLATION METHOD

According to this method, the non-polymerizable Formula II component which may be a common solvent like toluene or even can be a preformed dimer not capable of further polymerization such as 1,3-diphenyl cyclobutane is first charged to the reaction vessel to serve as a diluent reactant. The catalyst may then be suspended therein. Since the immediate reaction comprising either alkylation or dimerization will take place with a polymerizable reactant, the Formula I component is added only dropwise, so that it is immediately diluted by the Formula II diluent and reacts therewith catalytically. By this method the polymerizable component is maintained at a very low concentration in Formula II reactant diluent and the reaction is largely alkylation of the diluent. Small amounts of dimer may also be formed and such may ultimately re-enter the alkylation reaction.

B. COMBINED ALKYLATION AND DIMERIZATION

According to this procedure, the polymerizable component is not particularly protected from substantial polymerizing, but rather both polymerization of the Formula I compound as well as alkylation of Formula II takes place.

Thus, both types of compounds are charged to the reaction vessel together with catalyst, so that large amounts of dimerization take place forming dimers which in turn may ultimately enter into the alkylation reaction either as a Formula I or Formula II compound, since both types may be formed in the dimerization. Of course, a large portion of the reaction is direct alkylation of Formula II by Formula I compound without dimerization.

C. CONTROLLED CATALYST ADDITION

A third procedure is that of forming a mixture of Formula I and Formula II compounds in any selected of a wide range of proportions and adding the catalyst slowly and gradually to the mixture. The reaction is controlled approximately by the rate of catalyst addition. Again, both dimerization and alkylation takes place as in B.

It will be appreciated that combinations of these methods can be applied, for example, any of methods A, B and C may be modified by further addition of diluent Formula II added at intermediate stages as the reaction proceeds, to continue the degree of alkylation if desired.

The examples of Tables II and III discussed hereinafter illustrate the results and conditions of these two methods.

The preferred method of the present invention involve alkylation of a benzene ring with a single aromatic alkene such as styrene or alkylstyrene, or a cyclic hydrocarbon diene such as divinylbenzene. It is prefered that at least one of said cyclic groups, e.g. phenyl groups, be an alkylated group as defined hereinbefore employing an alkylating catalyst which may be an aqueous acid catalyst, usually a strong mineral acid like sulfuric, phosphoric and/or hydrofluoric acid, or an anhydrous Lewis acid, e.g., like $AlCl_3$, a boron halide or boron fluoride or their complexes, such as boron fluoride-phenylate, boron fluoride-etherate, boron fluoride dissolved in sulfuric acid, boron fluoride dissolved in phosphoric acid, and other acid alkylation and condensing agents with or without the Friedel-Crafts type catalysts. Usually a Friedel-Crafts type catalyst such as aluminum chloride may be used alone to produce a mixture of dicyclic and tricyclic precursors represented by Formula III.

When using sulfuric acid as a catalyst, the usual alkylating strength is above about 90%, but generally below about 98%, above which sulfonation of the aromatic rings, or excessive condensation to polycyclic compounds may begin to occur.

Particularly, such aforesaid catalysts are used to react an aryl hydrocarbon with an unsaturated aryl hydrocarbon derivative carrying unsaturated group in one or more substituent aliphatic groups.

In producing the high-gravity and high-energy fuels of my invention, such as by the alkylation of an aryl ring of an arylhydrocarbon of Formula II by reaction therewith of an aryl olefin, aryl diolefin, alkylarylolefin or alkylaryldiolefin or analogous cycloalkyl olefines of

Formula I in the presence of a catalyst selected from the class of Friedel-Crafts catalysts and Lewis acids, followed by hydrogenation, compounds of Formula IV having C_{14} to C_{30} form the preferred liquid fuels. Higher than C_{14} to C_{30} products may be formed simultaneously in minor amounts, and where a fuel of improved viscosity is desired the higher boiling products can be readily separated therefrom as residue from distillation under reduced pressures.

The specific gravity of such liquid mixtures will generally exceed about 0.85, and by the term "high gravity" as used herein, I mean a liquid having this minimum or higher gravity. The B.t.u. value exceeds 130,000 B.t.u. per gallon and will usually exceed about 135,000 B.t.u. per gallon and by the term "high energy" as used herein, I mean a combustible mixture having this minimum of 130,000 or higher B.t.u. value per gallon. For instance, the gravity of the jet fuels hereof usually lie in the range of about 0.88 up to about 0.94, and the B.t.u. value preferably ranges from about 135,000 up to about 145,000 B.t.u. per gallon.

Typical compositions produced by the process of the present invention are mixtures of hydrocarbon compounds comprising di- and tricyclic compounds, the dicyclic compounds including, for example, di-(tetra methyl-cyclohexyl)-1,1-ethane or (isopropyl-cyclohexyl)-cyclohexyl-2,2-propane, di-(dimethyl-cyclohexyl)-1,1-hexane and the tricyclic compounds including for example, (methyl-isopropyl-cyclohexyl)-cyclohexyl-cyclohexane, di-(cyclohexylethyl)-cyclohexanes, and the poly-cyclic compounds including, for example, mono- and poly-methyl-cyclohexyl-perhydroindans, and (cyclohexyl-propyl)-cyclohexyl-perhydroindans, said mixtures of hydrocarbon compounds preferably having 14 to 30 carbon atoms, and being formed by (a) alkylation of a Formula II hydrocarbon with Formula I hydrocarbon followed by hydrogenation and (b) simultaneous dimerization of the Formula I component, followed by hydrogenation.

The dimers of the Formula I reactant or codimers of two arylolefin reactants including self-alkylation products which are hydrogenated to saturated high energy compounds, are always present in at least minor amounts in the reaction products when an arylhydrocarbon is alkylated with an aryl olefin employing acid catalysts such as acids of the Lewis types and Friedel-Crafts type catalysts and since they contribute to the high fuel value as well as aiding in lowering the melting point of the fuel mixture, they may be left in the fuel mixtures, if so desired. However, by crystallization and distillation they may be separated either from the Formula III composition or from the final hydrogenation product.

Two molecules of the vinyl or alkenyl aromatic or cyclo-alkyl reactants, Formula I types can react together to give intermediate dimers which are hydrogenated to saturated fuel components of this invention. Thus styrene with certain procedures of the present invention employing a Friedel-Crafts catalyst, or sulfuric, phosphoric and like acids can react with itself to give mixtures comprising the following precursors for hydrogenation.

When o-, m-, and p- alkyl ring substituents are present together in the vinylaromatic hydrocarbon (Formula I types), it is obvious that additional dimers and codimers of the vinyl component increase still further the number of components in the final hydrogenated fuels of this invention.

As already exemplified the vinylaromatic compound can self-alkylate, e.g., one molecule of styrene can alkylate the aryl ring of a second molecule of styrene giving o-, m- and p-phenylethylstyrene which upon partial hydrogenation produces o-, m- and p-ethyl (diphenylethane) represented by the formula

$$C_2H_5—C_6H_5—C_2H_4—C_6H_5$$

Practically the fully hydrogenated styrene dimers and the dimers of alpha-methylstyrene also can serve as high energy fuels both in mixtures of Formula IV compounds in which they form, or when separated. For example, the 1,3,3-trimethyl-1-phenylindane, above noted, was prepared and isolated in minor amounts from the alkylation of ethyltoluene with styrene by concentrated sulfuric acid at 0–5° C. After hydrogenation, it showed a heat of combustion of 18,400 net B.t.u./lb. and 142,425 net B.t.u./gallon, while the alkylation product of styrene and ethyltoluene containing small amounts of this dimer, after hydrogenation, gave a fuel net combustion value of 18,465 B.t.u./lb. and 143,500 B.t.u./gallon.

As previously mentioned, one of the practical advantages of the present invention is that low-cost commercially available feed stock can be utilized to produce the high energy fuels desired. Large tonnages of styrene are required for the rubber and plastic industries. In the manufacture of styrene, ethylbenzene is produced by ethylation of benzene and dehydrogenation of the resultant ethylbenzene or a C_8 cut rich in ethylbenzene is employed. In a typical process (see "Styrene," by Boundy and Boyer, Reinhold Publishing Corp., New York, 1952) 16 lbs. ethylene and 78 lbs. of benzene are reacted (in the alkylator) at 95° C. in the presence of a Friedel-Crafts catalyst, e.g., $AlCl_3$ with hydrogen chloride or methyl chloride activator, to produce 43.5% ethylbenzene, 40% benzene+16.5% polyethylbenzene. The hydrocarbon product is washed and fractionated to give ethylbenzene of over 99% purity, together with benzene and polyethylbenzenes. The latter are recycled to the alkylator where the benzene is alkylated to ethylbenzene and the polyethylbenzenes are de-alkylated to ethylbenzene. The ethylbenzene of 99% purity is then dehydrogenated over metal oxide catalysts, e.g., combinations containing magnesia or iron oxide, in the presence of steam at about 600° to 660° C. The dehydrogenated product is cooled, the gas stream (containing hydrogen, carbon monoxide, carbon dioxide, methane and ethane) is refrigerated for recovery, the water layer separated, and the hydrocarbon product shows a typical average composition of: 37% styrene, 61.1% ethylbenzene, 1.1% toluene, 0.6% benzene, 0.2% tar, a mole ratio of less than 2/1 for Formula II/Formula I compounds.

Ordinarily this product stream is fractionated under low pressures to obtain the purified styrene for the rubber and plastics industry, but in the present invention, it may be fed without further treatment to an alkylator as described above using strong acids or Friedel-Crafts type catalysts and the styrene alkylates the benzene, toluene and ethylbenzene and at the same time the styrene in part is dimerized and self-alkylated. The dimers in turn are partially alkylated by styrene. If it is desired to overcome the relatively high dimerization and to improve the yields of bicyclic hydrocarbons, the dimer formation can be maintained at a low level. Therefore, it is advantageous to dilute this styrene-ethylbenzene, toluene-benzene mixture with benzene and/or ethylbenzene so that the entering feed may comprise about 15 to 25% styrene in the alkylation feed, or a mole ratio of Formula II/Formula I compounds of about 4. An easier more economical method of obtaining the feed stock of the present invention is to increase the feed rate of the ethylbenzene in the above described dehydrogenation step in the manufacture of the styrene. By this procedure a composition having the desired styrene content, for example, 20% styrene, 78.5% ethylbenzene, 1% toluene and 0.5% benzene may be obtained. Such feed mixture, alkylated according to the present invention, gives high yields of high energy fuels, the styrene then being utilized to the extent of about 95% in alkylation of the ethylbenzene, toluene, and benzene and about 5% in dimerization when typically using concentrated sulfuric acid catalyst at 0–5° C. The resulting alkylation product after hydrogenation yields a fuel of over 140,000 B.t.u./gallon (net energy of combustion).

Similarly vinyl toluene for the plastics industry is manufactured by the steps of ethylation of toluene to form o-, m- and p-ethyltoluenes, separation of the o-isomer and dehydrogenation of the m- and p-ethyltoluene mixture. The effluents comprising chiefly vinyl toluenes (45%) and ethyltoluenes (about 53%), together with small amounts of benzene, toluene, ethylbenzene, styrene, xylenes and tar. This mixture as feed for the present invention need not be purified but may be fed directly to the alkylation reactor to form the fuel precursors of the present invention which by hydrogenation yield high energy fuels of 135,000 to 145,000 B.t.u./gallon. However, as with styrene, the reaction mixture may be adjusted to a lower vinyltoluene content such as about 20% as desired, to increase vinyltoluene alkylation of ethyltoluene and to decrease dimerization of the vinyltoluene by the Lewis acids or Friedel-Crafts alkylation catalyst. This said 20% composition may be obtained by dilution with toluene, ethyltoluene, cumene and the like, or it may be obtained by operating the ethyltoluene dehydrogenation step at a faster feed rate in manufacturing the vinyltoluene.

Moreover, in production of vinyltoluene for use as feed in the present invention, the ortho-ethyltoluene isomer need not be removed from the m- and p-isomers or other C_9 aromatics prior to dehydrogenation. The reason for its removal in commercial production of vinyltoluene is that dehydrogenation of o-ethyltoluene gives, besides o-vinyltoluene, considerable indene formation not desired in the vinyltoluenes utilized in aromatic vinyl plastic field. However, when the vinyltoluene is used in the present invention, the indene impurity or component is useful both as (a) an alkylatable hydrocarbon which thus can react with vinyl toluene and (b) an aromatic olefin which can alkylate ethyltoluene, and other aromatic components present.

Indene gives by alkylation of ethyltoluene, for example, indanylmethylethylbenzene (10 isomers) whereas each vinyltoluene (o-, m- and p-) alkylates indene to some extent to produce four isomers each similar to the dimers above. These indene and/or indanyl compounds are not represented by Formula III but may be left in the precursors since hydrogenation thereof gives high energy compounds.

Again crude alpha-alkyl styrene such as alpha methyl styrene in mixtures with the parent branched alkylbenzene such as cumene is produced commercially. For example, about 40% alpha-methylstyrene is obtained together with cumene (about 56%), the remainder being benzene, toluene, styrene and tar, by dehydrogenation of cumene over metal oxides such as MgO or Fe_2O_3 catalysts at 600° C. to 675° C. Without fractionation this mixture is fed to the alkylation catalyst, for example, BF_3—H_3PO_4 catalyst, or concentrated H_2SO_4 catalyst and the like, to produce a precursor mixture of bicyclic and tricyclic isomeric Formula III hydrocarbons which when hydrogenated shows a net energy of combustion over 142,000 B.t.u./gallon. Again, to decrease the formation of tricyclic and polycyclic hydrocarbons, it may be desirable to reduce the alpha-methylstyrene content of the feed either by dilution of the dehydrogenation effluents (from manufacture of alpha-methylstyrene) with cumene, or to operate the dehydrogenation step at a higher feed rate so that the feed contains from 15 to 25% alpha methyl styrene. Similarly other alkyl and dialkyl aromatic hydrocarbons may be partially dehydrogenated by the same or similar processes to produce desirable alkylation feed mixtures of Formula I, and Formula II compounds for the present invention. Such suitable feeds for dehydrogenation are methyl cumenes, ethylcumenes (ethyl isopropyl benzenes), diethylbenzenes, n-butyl benzenes, 1-methyl-1-phenylbutane) (i.e., 2-phenylpentane), C_7 to C_9 aromatic petroleum fraction (mixture of C_7 to C_9 aromatic hydrocarbons), 2-phenyldodecane, a C_8 petroleum aromatic fraction (as obtained by extracting aromatics from a C_8 petroleum fraction or by synthesis from C_8 alkanes and alkenes, and extraction of products) and the like.

It is inherent in the present invention that fuels of lower melting points and viscosities are obtainable as a result of the fact that said fuels can comprise mixtures of dicyclic alkane hydrocarbons, a major portion of which are position isomers from hydrogenating the alkylated aromatic hydrocarbons, and the remainder being homologous hydrocarbons of 1 to 4 higher or lower carbon count together with hydrogenated dimers and codimers from the vinyl aromatic hydrocarbons.

The reaction of styrene with toluene followed by hydrogenation produces a mixture of three isomers comprising 1-(ortho-, meta- and para-methylcyclohexyl)-1-cyclohexylethane together with 1,3-dicyclohexylbutane, 1,3-dicyclohexylcyclobutane, and 3-methyl-1-cyclohexylhydroindan (the latter three being hydrogenated dimers). The mixture of all of these components in both cis and trans forms is a rather narrow boiling range fuel (275–281° C./745 mm. Hg). The viscosity and melting point may be lower still if the mixture of isomers is broadened by inclusion of benzene and xylene in the toluene starting material i.e., a C_6–C_9 aromatic petroleum fraction, for reaction with styrene without excessive increase in boiling range. Thus 25 pts. by weight of each of benzene, toluene, xylene and styrene by reaction in the presence of 10 pts. by wt. 97% H_2SO_4 at 5° C. gave a mixture of Formula III precursors which, when hydrogenated, boiled at 265–288° C. The carbon atom content of the mixed isomers and homologues ranged from 14 to 16. Up to 20 parts by weight tricyclic products may be retained in these dicyclic fractions without loss of fluidity or B.t.u. value.

If it is desired to increase the styrene dimer content of the precursors for the hydrogenated fuel, such as, the dicyclohexyl-butane and 1-methyl-1-cyclohexylhydroindan components of the high energy fuel mixture, the methods outlined above under B and C, such as use of a high styrene content in the styrene-aromatic feed mixture for the Lewis acid or Friedel-Crafts alkylation or addition of the catalyst to the premixed Formula I and Formula II feed components, or the use of sulfuric, phosphoric or sulfonic acids in concentrations less than 90 wt. percent in water, in contrast to the slow addition of Formula I to the catalyst Formula II mixture. Thus a 1:1 ratio of toluene-styrene feed gives the dimer as the major component (about 90%) of the product when the H_2SO_4 catalyst is stirred into it. On the other hand, if the ratio of toluene to styrene is kept quite high by gradually adding the styrene to the aromatic hydrocarbon-sulfuric acid catalyst mixture, the dimer content of the product can be kept below 10% or even below 5%. The successful application of these procedures to control the quality of dimer formation is based on the facts that (a) alkylation catalysts also catalyze the dimerization of vinylaromatic compounds such as styrene, vinyltoluene, alpha-alkylstyrene and the like, (b) the rate of dimerization is more rapid than the rate of alkylation, (c) and compensation can be made for the higher rate of dimerization by maintaining a low concentration of the vinylaromatic hydrocarbon in the alkylatable hydrocarbon in accordance with the laws of mass action. The preferred composition of the feed mixture is from 20 to 30 weight percent of vinyl aromatic hydrocarbon (Formula I) and 30 to 70 weight percent saturated alkylatable aromatic hydrocarbon of Formula II when it is desired to produce fuels therefrom.

As formed by the methods herein, the high energy compounds of this invention constitute mixtures of hydrocarbons including position isomers, having from 14 to 30 carbon atoms. In its simplest form, fuel obtained from reaction of styrene and benzene, e.g., with 90% sulfuric acid catalyst followed by hydrogenation, will contain chiefly dicyclic compounds, 1,1-dicyclohexyl ethane (from alkylation), 1,3-dicyclohexyl-butane and

-cyclobutane (from dimer formation), each of these occurring in a cis and trans form; together with lesser amounts of tricyclic compounds.

A less simple mixture obtained by the present invention is obtained from toluene and styrene, e.g., with concentrated sulfuric acid catalyst, followed by hydrogenation, wherein the three position isomers 1-cyclohexyl-1-(o-, m- and p-methylcyclohexyl)-ethane, are obtained from the initial alkylation reaction, and the 1,3-dicyclohexyl-butane and -cyclobutane and 1-methyl-1-cyclohexyl-hydroindan from the styrene dimerization reaction. When a mixture of xylenes (o-, m- and p-) are similarly reacted with styrene and the products hydrogenated, the resultant high energy fuel contains 6 position isomers of 1-cyclohexyl-1-(dimethylcyclohexyl)-ethane in addition to the said butane and indan derivatives arising from the dimerization of styrene. The six position isomers arise from the different position of the two methyl groups in the precursor xylyl substituents in the 1-phenyl-1-xylyl-ethane, the alkylation product of styrene and the xylenes. The relative amounts of the six isomers present are determined by the relative activities of the hydrogens on the xylene nuclei in the presence of the catalyst under the conditions of temperature and catalyst employed.

Thus the number of individual components present in the final hydrogenated fuel increases with the number of identical alkyl substituents in the Formula II hydrocarbon; still more individual hydrocarbon products result when the two or more alkyl groups of the Formula II reactant are different, e.g., a mixture of methyl-ethylbenzenes (i.e., ethyltoluenes) reacted with styrenes, and hydrogenated, leads to a fuel having besides the several hydrodimer components, ten position isomers of 1-cyclohexyl - 1 - (mehtyl-ethylcyclohexyl) - ethane. Trimethyl benzenes and styrene give six position isomeric 1-cyclohexyl-1-(trimethylcyclohexyl)ethanes in the final fuel, while dimethylethylbenzene gives 19 position isomers in the final fuel besides the components deriving from the styrene dimer.

Moreover, as described below some of the cyclic radicals themselves are often derived from hydrocarbon fractions comprising multi-component mixtures of alkyl substituted aromatic hydrocarbons, e.g., a C_6 to C_9 aromatic reformate, from which the final products hereof may be made, and, as thus formed, may comprise mixtures of even greater complexity.

In the case of alkylation of the Formula II hydrocarbons with alpha-alkylstyrene the four reported hydrodimers will be present in addition to the position isomeric products. The six fuel components arising from the dimers are:

2,4-dicyclohexyl-2-methylpentane
1,3,3-trimethyl-1-cyclohexyl-hydroindan
1,3-dimethyl-1,3-dicyclohexyl-cyclobutane and
o-, m- and p-(2-cyclohexylpropyl)-isopropyl-cyclohexane (from self alkylation)

Another variation of the present invention utilizes a mixture of two or more vinylaromatic compounds (i.e., aromatic olefins) to alkylate an alkyl substituted aromatic hydrocarbon or mixtures of two or more aromatic hydrocarbons such as C_7–C_9 aromatic petroleum fraction. The hydrogenated products from such alkylation include the four types of above mentioned hydrodimers from each vinylaromatic monomer i.e., the dicyclohexyl-alkanes, cyclohexyl substituted hydroindan derivatives, and dicyclohexyl-cyclobutane derivatives, along with codimers obtained from each possible pair of feed vinylaromatic hydrocarbon.

Thus my compositions may comprise mixtures of a great number of components including hydrodimers and hydrocodimers of styrene and alkyl substituted styrenes, position isomers of hydrogenated alkylated aromatic hydrocarbons together with homologues thereof, as formed by the methods described hereinafter. This complex composition is desirable because as a mixture it allows the production, for example, of a jet fuel usually in liquid form when the carbon atom content is in the range of 14 to 30, a product of relatively high boiling point, relatively constant high gravity, and at moderate temperatures, fluid viscosity. My mixture including numerous position isomers has also a relatively low depressed freezing point, often as much as 50° C. below that of any of the corresponding pure components which are present in the mixture.

Another fuel of relatively simple composition of particular interest from the standpoint of thermal stability is available from the present invention by alkylation of benzene with alpha-methylstyrene followed by complete hydrogenation, such fuel comprising a mixture of 2,2-dicyclohexyl - propane, 1,3 - dimethyl - 1,3 - dicyclohexyl-cyclobutane; 2-methyl-2,4-dicyclohexyl-pentane, 2-(o-, m- and p-isopropyl-cyclohexyl)-2-(cyclohexyl)-propane and 1,3-trimethyl-1-cyclohexyl-hydroindan and constituting a liquid fuel, when the tricyclic hydrocarbon products are removed therefrom.

When a mixture of aromatic hydrocarbons, e.g., C_8 aromatic petroleum hydrocarbon extract fraction containing the three xylenes, ethylbenzene and toluene is used instead of benzene, a quite complex mixture of products results by alkylation with styrene or a substituted styrene, such as alpha-methylstyrene, vinyltoluene and the like followed by hydrogenation. Besides the position isomers present from each alkyl benzene and dialkylbenzene there are the four hydrodimer types and when a mixture of substituted styrenes is used, e.g., the three vinyltoluenes, to alkylate a mixture of aromatic hydrocarbons there are many more position isomers present in the product along with a mixture of 18 hydrodimers and hydrocodimers.

Even though there are some symmetrical "bis" compounds present in certain of my fuel mixtures, any one of these can be present only as a small portion of even the simplest of the complex mixtures. Thus a fuel prepared from p-methylstyrene by alkylation of toluene, followed by hydrogenation contains a minor amount of 1,1-bis-(p-methylcyclohexyl)-ethane.

For further example, the di-(ethylcyclohexyl)-ethanes formed by condensation of a divinylbenzene (containing o-, m- and p-divinylbenzene) with ethylbenzene, followed by hydrogenation, results in (1) six isomers of Formula III, in addition to (2) sixteen hydrogenated isomers resulting from self-condensation products (i.e., self-alkylation products) of divinyl benzene, (3) many hydrodimers and hydrocodimers, and (4) the many tricyclic compounds of Formula III in minor amounts. Similarly a mixture of the three divinylbenzenes reacted with the synthetic xylene mixture described hereinbefore, gives, after hydrogenation, chiefly 18 isomers of 1-(ethylcyclohexyl)-1-(dimethylcyclohexyl)-ethanes in addition to lesser amounts of 1-(ethyl-cyclohexyl)-1-(methyl cyclohexyl)-ethane isomers, 1,2-di-(ethyl-cyclohexyl)-ethane isomers, six isomers of di-(ethylcyclohexyl)-cyclobutane and six isomers of di-(ethylcyclohexyl)-butanes, many hydrocarbons resulting from self-condensation of divinylbenzene and many isomers of tricyclic compounds.

A further advantage of my mixture of position isomer compounds is that they may be produced to desirably close specifications, most desirable for a jet fuel, notwithstanding that they are a mixture of so many distinct compounds, by methods which in themselves are highly economic.

As pointed out, the total number of carbon atoms is in the range of 14 to about 30 where my compounds are used as normally liquid fuels at ambient temperatures. Within these limits, the alkyl and alkylene substitutions of the benzene radicals will be selected in number and size whereby bicyclic liquid compounds are produced. For example, the alkane group (arising from the vinyl or alkenyl group of Formula I) can be reduced in carbon chain size, preferably in the range from 2 to 5 carbon

atoms, while simultaneously the alkyl groups attached to the rings of Formulas I and II can be increased in number and size, and vice versa (e.g., the alkane portion can be increased by use of alpha-alkylstyrene to alkylate benzene and alkylbenzenes, the alkyl of the substituted styrene being from C_1 to C_{10} alkyl) for purposes of maintaining the size of the compounds within the 14 to about 30 carbon atoms limits to define a liquid fuel.

Similarly the feed constituents can be selected to form a liquid fuel containing tricyclic components e.g., a synthetic xylene mixture reacted with styrene in the presence of BF_3. phenolate catalyst at 0–5° C. followed by hydrogenation of product gave a liquid fuel distilling at 295° C./745 mm. to 245° C./2 mm. which contained 40% tricyclic components having 24 carbon atoms.

Outside of these limits of 14 to 30 carbon atoms, my mixture of isomeric compounds can be a viscous oil or a solid mixture of components including position isomers. These too can be used as fuel, but for use as liquid fuel they may have to be heated to melt them or to reduce their viscosity. These, as well as the normally liquid types, have other uses as stated above.

An advantage of the variation of my liquid fuel in the range 14 to about 30 carbon atoms, and the variation to produce a mixture of numerous isomeric and homologues components and usually including a large number of position isomers in each product is that my mixture can be made relatively uniform with respect to the number of carbon atoms of each product in any of its uses. For instance as set forth in many of the examples below each product may be composed of a mixture of compounds of the same number of carbon atoms. When the ring substituents are derived from a commercial mixture of C_7 to C_9 aromatics obtained as a total aromatic petroleum extract or even a select fraction thereof, the total carbon atom count in the several compounds of the resulting mixture varies only in a narrow range for liquid fuels. Of course, side reactions such as further condensation, produce compounds having a higher number of carbon atoms such as the tricyclic and polycyclic alkanes, for example, the di-(alkylcyclohexyl-propyl)-alkylcyclohexane, and the like. The polymeric multiring compounds being higher boiling are readily separated by distillation. Where a wide boiling range fuel is not objectionable and where the final products are highly viscous liquids or even solids, such heavy ends need not be removed from the fuel. These heavy ends of course are also represented by the Formula IV.

The above discussion has been chiefly devoted to conditions preferred for producing the high energy fuels of this invention in high yields wherein the preferred feed composition comprises at least two moles of Formula II compound for each mole of monovinylaromatic hydrcarbon. (Formula I), and at least four moles of Formula II compoud per mole of divinylaromatic hydrocarbon, and at least 6 moles of Formula II compound per mole of trivinyl compound, etc.

There are uses for partially or fully hydrogenated products of this invention which may comprise a major portion of hydrodimers and codimers. For such products it is preferred to employ feed compositions consisting of mixtures of Formula II and Formula I compounds in mole ratios of less than 2/1; in some cases dimers, e.g. alpha-methylstyrene dimers including self-alkylate may be desired for hydrogenation, with no other alkylation products being present. Such hydrogenated products and their Formula III precursor intermediates find special uses as lubricants, plasticizers, hydraulic fluids, power transmission fluids and the like.

The present invention discloses the process of preparing new mixtures of isomeric dicycloalkyl- and tricycloalkyl-alkanes and di- and tri-cycloalkyl-cycloalkanes and alkyl derivatives thereof prepared by extensively hydrogenating products prepared by using Lewis acid catalysts and starting with the aromatic olefin reactant Formula I comprising a cyclic hydrocarbon substituted with olefin or alkenyl groups, and reactant Formula II aromatic hydrocarbon, to form the precursors for hydrogenation. Alkylation reactions techniques, as known in the art, generally are employed herein at ambient temperatures and sometimes lower temperatures, such as 0° C. to −30° C. and including certain catalysts such as hydrogen fluoride which can operate at temperatures considerably below ambient temperatures such as −20° C. to −92° C.

Typical of Formula II reactant as alkylphenyl producing groups are: toluene, the ortho, meta or para xylenes and their mixtures, the trimethylbenzenes including mesitylene, durene, ethylbenzene, the di- and tri-ethyl benzenes, the methylethyl benzenes, the dimethylethyl benzenes, the diethylmethyl benzenes, the diethyl-dimethylbenzenes, the mono-, di-, and tri-propyl benzenes, the n-butyl, sec-butyl, isobutyl, and tert-butyl benzenes, the isopropyl benzenes including cumene and pseudo-cumene, diisopropyl benzene, dibutyl benzenes, mono and diamyl benzene, and mono- and di C_6-alkyl benzene, mono C_7-alkyl to dodecyl benzene, with mixed alkyl groups including those with both normal and branched C_1 through C_{12}, preferably C_1 to C_5 alkyl substituents, and the various combinations of alkyls with the limitations of Formula II.

The vinyl hydrocarbon alkylating group (Formula I) can be styrene, alpha-methyl styrene, alpha-alkylstyrene up to alpha-decyl styrene, o-, m- and p-vinyltoluene, o-, m-, and p-vinylethylbenzene, o-, m-, and p-methyl-alpha-methylstyrene, divinylbenzene, trivinylbenzene and the like.

In commercial practice an aromatic extract of a reformation or aromatization reaction (termed petroleum reformate) may be used in its entirety as reactant usually comprising the C_6 to C_9 aromatics which may also contain up to 50% benzene, or select C_7, C_8 or C_9 aromatic fractions of such extract may be used or in combinations. The C_8 fraction comprising the three isomeric xylenes and ethyl benzene sometimes contaminated with toluene and/or with some C_9 aromatics may be most economically used in its entirety. This valuable C_8 aromatic fraction may often first be distilled to separate the ortho-xylene isomer leaving the mixed meta- and para-xylene isomers. The latter fraction can have its para-xylene extracted for even more valuable uses (such as oxidation to terephthalic acid), and the ortho- and meta-xylenes fractions recombined for use herein. Any of these select xylene fractions or the entire C_8 fraction, are useful in the practice of this invention. Thus any petroleum refinery reformate having an economically recoverable quantity of aromatics may comprise a useful source material from which an aromatic extract may be obtained and used as a source of the alkyl benzenes, either as a whole extarct, or as select fractions thereof. A typical preferred C_8 fraction may comprise about 2% toluene, 10% p-xylene, 48% m-xylene, 19% o-xylene and about 21% ethylbenzene.

In carrying out the alkylation reaction, where predominantly the bicyclic compound is desired, the alkyl benzene is usually used in substantial excess, e.g., a 2 to 3 times molar excess in relation to the equivalent quantity of alkylating group material (vinyl equivalent of Formula I) employed and where higher polycyclic side reaction compounds (such as included in Formulae III and IV), a lower ratio down to about 0 to 2 moles of Formula II compound per equivalent of alkylating compound (Formula I) is used. The catalyst may be usually added thereto at below room temperature, and if the alkylating compound is difficult to react, the temperature may be raised; if the alkylating compound is highly reactive, the temperature may be lowered, applying cooling or refrigeration as needed, and the alkylating group material is usually added slowly, such as dropwise over a several hour period, usually 2 to 12 hours, with continued

agitation in order to avoid excess side reactions thereof, the conditions being modified depending on the activity of the reagents, and on the desired product.

When the alkylation reaction does not terminate by joining of only two ring groups, it is preferred for high yield of fuels, to allow the reaction to convert only a portion, such as about ⅓ of the available alkyl benzene, to the Formula III compound before terminating the reaction. The reaction products (Formula III compounds containing minor amounts of dimer or dimer derived compounds) are then recovered from the reaction mixture and the excess unreacted compounds such as alkyl benzene are recycled to the reactor.

Formula I compounds containing two functional groups such as divinylbenzene can result in both mono- and dialkylation, i.e., alkylation of two aromatic nuclei, in the same reaction in the presence of the selected acid or Friedel-Crafts catalyst.

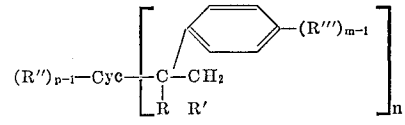
In the instance of reacting in the presence of aluminum chloride catalyst or an equivalent Friedel-Crafts catalyst, the alkyl benzene compound (Formula II), and the divinylbenzene as reactant (Formula I) are first mixed, and the mixture usually is cooled to from —70 to 0° C., and then the aluminum chloride can be added in any suitable manner, even rapidly, with or without a promoter. The reaction mixture is maintained at below —5° C. for 1 to 5 hours and is then permitted to warm up gradually to 25° C. over a period of 1 to 2 hours to complete the reaction.

After the position isomeric compounds of Formula III together with the position isomers, codimers and dimers (from Formula I compounds) are prepared, they are freed of catalyst residues by decantation, filtration and/or water washing with or without the aid of acid for Friedel-Crafts catalysts removal, followed by an alkaline aqueous wash; or in the case of the acid catalyst, catalyst removal is accomplished by washing with only water and/or alkaline aqueous wash. In most instances the unreacted starting materials are removed by distillation, the distillate having traces of water present from the washing; the distillate after drying, e.g., with silica gel, calcium sulfate, and the like is recycled back to feed tanks for the alkylation process. The product compounds remaining from said distillation are then hydrogenated. Before hydrogenation, the Formula III product may be further distilled for greater purity to separate the tricyclic and polycyclic compounds therefrom; or the tricyclic and polycyclic compounds may be hydrogenated therewith and separated, if desired, from the hydrogenated product. The hydrogenation is usually carried out in a diluent, e.g., a paraffin solvent such as pentane or hexane, or a cycloalkane solvent such as cyclohexane or methylcyclohexane in the presence of a hydrogenation catalyst for aromatic compounds, etc. In the examples herein an active Raney nickel or Raney cobalt catalyst was preferred.

In order that hydrogenation of the aromatic rings of Formula III compounds proceed at a reasonable rate, hydrogen is employed at non-critical elevated pressures, usually from about 500 p.s.i. to 5,000 p.s.i. To hydrogenate these aryl compounds, the temperature is raised non-critically above a minimum temperature, usually 100–200° C., but sometimes higher, until hydrogenation commences. When the Formula III compounds contain unsaturation other than aromatic unsaturation such can first be removed by hydrogenation under mild conditions (below 100° C.) to yield intermediates which can have use as plasticizers, extenders, hydraulic fluids etc. and these materials can, of course, be exaustively hydrogenated to form the polycyclic alkanes hereof. In such hydrogenation, each aryl ring usually has a minimum or threshold hydrogenation temperature which must be exceeded and this depends on the activity of the catalyst employed and on the position of the alkyl substitutents in the individual aryl rings.

By control of catalyst activity, temperature, hydrogen pressure and selection of solvent, I can obtain selective hydrogenation, i.e., I can hydrogenate only a single aromatic ring of these bi-aromatic ring compounds, e.g., of Formula III, thus producing compounds in which each alkenyl group of R′, R, R″ and R‴ of Formula III have been converted to alkyl and some, but not all, of the aromatic groups of Ar, or included in the Formula II radical of Formula III, have been hydrogenated to a cycloalkane group. Thus the Formula III product can have all side chains and either the benzene group of Formula I, or Formula II hydrogenated to a cycloalkane group, but not both, as illustrated in the formulae comprising a mixture of position isomers having the formula:

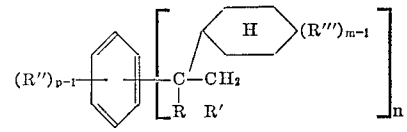
FORMULA V



wherein Cyc in this formula is 5 to 6 carbon atom cycloalkane, R and R′ are members of the group consisting of alkyl and Cyc-alkyl which together with the ethyl group have 2 to 12 carbon atoms, R″ is a member of the group consisting of alkyl, and Cyc-alkyl, R‴ may be alkyl, Cyc-alkyl, Cyc-cycloalkyl, indanyl and alkindanyl, each of the hydrocarbon radicals R″ and R‴ having from 1 to 12 carbon atoms, *m* is an integer of 1 to 5, *n* is an integer of 1 to 2 and *p* is an integer of 1 to 4.

Alternatively the intermediate hydrogenation product is a mixture of position isomers having the formula:

FORMULA V



where R, R′, R″, *m*, *n* and *p* in this formula are the same as in Formula V, but R‴ is a member of the group consisting of alkyl, hexhydro indanyl, alkhexhydro indanyl and Cyc-cycloalkyl where Cyc is a member of the group consisting of 5 to 6 carbon atom cycloalkane and benzene radicals, the hydrocarbon radicals of R‴ having from 1 to 12 carbon atoms. The intermediate hydrogenation composition of Formula IV may be mixtures of isomers of both Formulas V and VI.

Moreover, dimers occurring in the Formula III product, if desired, can be only partially hydrogenated with the total Formula III product or after separation therefrom. For example, in the instance of styrene, the following dimers occur (1) 1-3-diphenyl butene-1, (2) 1,3-diphenyl butene-2, (3) 3-methyl-1-phenyl-indane, (4) 1,3-diphenyl cyclobutane, (5) o-, m-, p- (2 - phenyl ethyl) styrene, which by partial hydrogenation can be converted respectively to (1) 1,3-diphenyl-butane, 1-cyclohexyl-3-phenyl butane, and 1-phenyl-3-cyclohexyl butane, (2) the same, (3) 1 - phenyl - 3 - methyl - 4,5,6,7,8,9-hexa-hydroindan, and 3-methyl-1-cyclohexyl indan, (4) 1-cyclohexyl-3-phenylcyclobutane and (5) o-, m- and p- (2-cyclohexylethyl)-phenylethane and o-, m- and p- (2-phenylethyl)-cyclohexylethane and o-, m- and p- (2-phenylethyl)-phenylethane.

Where the vinyl benzene contains additional alkyl groups, these appear in corresponding positions of the homologous dimers, partially hydrogenated in the same way.

Thus, for example, the o-, m- and p- methystyrene dimers give four types of partially hydrogenated dimers corresponding to one ring hydrogenation only of the five dimers forms. Of course where olefinic unsaturation is present, the olefinic unsaturation is hydrogenated along with the first aromatic ring.

Similarly the tricyclic compounds of Formulae III

may be partially or stepwise hydrogenated so that only one or two of the three aromatic nuclei may be hydrogenated.

EXAMPLE 1

A typical specific exemplification of the preparation of isomers of the present invention is as follows: 500 pts. of a commercial xylene mixture of o-, m- and p-xylene containing some ethylbenzene and toluene is reacted with 100 pts. styrene which is added gradually over a period of 4 hours (e.g., using a sulfuric acid catalyst at 5° C.), followed by decantation, washing and distilling off unreacted starting materials, and hydrogenation in hexene over Raney nickel or Raney cobalt catalyst at 150° C. and 1,000 p.s.i. hydrogen, produces isomers of 1,1-(cyclohexyl)-(dimethylcyclohexyl)-ethanes in admixture with 1,1-(cyclohexyl)-(ethylcyclohexyl)-ethanes, di(cyclohexyl)- butane and -cyclobutane (from styrene dimerization), and cyclohexyl-methylhydroindan (from styrene dimerization), and numerous tricyclic compounds, the relative amounts of each isomer and individual component being dependent on the relative activities of the several different hydrogens of the hydrocarbons of the xylene fraction employed in relation to the dimerization rate of styrene.

It has been further found that the heat of combustion of such isomeric mixtures is partially dependent on variations in ratios of the amounts of respective isomers and components present. Thus, reaction of a commercial xylene with styrene at 5° C. with H_2SO_4 catalyst followed by acid removal and hydrogenation and from (b) reaction of the same commercial xylene with styrene at 5° C. with BF_3-phenolate followed by hydrogenation, contained different amounts of the various isomers and components and showed respectively 19,500 gross B.t.u./lb. and 19,815 gross B.t.u./lb. for the heat of combustion. Similarly reaction of styrene with xylene using anhydrous aluminum chloride as catalyst, followed by hydrogenation gave a fuel of 19,605 B.t.u./lb. Thus the broad fractions of a given position isomer mixture of di-(mono- or di-alkylcyclohexyl)-methane from two or more sources will differ in properties including the energy of combustion. The constancy of energy output of fuels from a given synthesis is an important advantage of the fuels of the present invention, particularly for rocket fuels since target calculations are based in part on the basis of known energy available from the fuel charge. The operating variables of the methods of synthesis of the fuels of the present invention are readily controlled to give a reproducible produce, hence reproducible heat of combustion.

By the reaction of styrene with a mixture of the three xylenes and three methyl-ethylbenzenes by the above described procedure followed by hydrogenation of the condensation product, there was obtained a fuel containing the hydrodimers of styrene in addition to a larger number of isomeric 1,1-(methylethylcyclohexyl)-(cyclohexyl)-ethanes and 1,1-(cyclohexyl)-(dimethylcyclohexyl)-ethanes, and the many di-(cyclohexylethyl)-cyclohexane position isomers; the various xylyl and ethylphenyl combinations as substituents for the phenylethane (in the styrene condensation product) thus increased the number of isomers obtained in the final hydrogenated products of this invention in comparison to the hydrogenated xylene-styrene reaction product also of this invention, and the freezing point was lower for the mixture containing the larger number of isomers.

The yields of precursors obtained in such alkylations of the present invention are highest when the amount of dimer formation is at a minimum. Thus when one mole of styrene is reacted with one mole ethylbenzene (molecular weights 104 and 106 respectively), the weight of the product is 210 grams. The theoretical yield is lowered considerably by dimer formation the total product of Formula III being decreased proportionate to the amount of dimer formation. Where all of styrene is converted to dimer the total yield becomes 104 g. Thus the yields will lie between 104 g. and 210 grams depending on the amount of dimer formation. The precursors (Formulas I and IV compounds) were hydrogenated over Raney nickel catalyst (e.g., Girdler's G–49 catalyst) using about 8 pts. by weight of methyl-cyclohexane, cyclohexane, hexane, or pentane as solvent for 1 to 4 pts. by weight of precursor. The hydrogenation was conducted at 100 to 200° C. under 60 to 100 atmospheres of hydrogen pressure in a batch reactor with agitation for 2 to 8 hours. The solvent was removed by distillation, the remainder being water white to light yellow fuels of this invention.

In the examples, the terms used are defined:

(a) By the term "gross heating value" of a fuel is meant the total heat developed on burning of fuel after the products are cooled back to the initial temperature (in present practice 75° F.), assuming that all the water produced by combustion is condensed.

(b) By the term "net heating value" of a fuel is meant the total heat developed on burning a fuel after the products are cooled back to the initial temperature (in present practice 75° F.) assuming the water of combustion is uncondensed.

Examples to demonstrate the practice of the present invention are set forth hereafter wherein at least one vinyl aromatic hydrocarbon (Formula I) in admixture with at least one saturated aromatic hydrocarbon (Formula II) was contacted with a Friedel-Crafts or Lewis acid catalyst. The reaction products consisting of Formula III compounds were separated from unreacted reactants and were hydrogenated. The pertinent physical properties were measured before and after hydrogenation.

EXAMPLE 1-A

Reaction of styrene with synthetic xylenes

A reaction kettle of 3-liter capacity was equipped with a mechanical stirrer, thermometer, and a dropping funnel. To the kettle was added 752 grams of synthetic xylene obtained from Sinclair Petroleum Company. The xylene had the following composition: 2% toluene, 10% p-xylene, 49% m-xylene, 19% o-xylene and 21% ethylbenzene. To the xylenes was added 0.1 mole of a boron fluoride-phenolate complex (General Chemical Division of Allied Chemical and Dye Corp.) containing 26% boron fluoride by weight. The mixture was stirred and the kettle cooled by immersing in an ice water bath.

Stirring was continued and 104 grams (one mole) of styrene was added dropwise over a period of 90 minutes at a rate adjusted to maintain a reaction temperature of 4±1° C. Stirring was continued for 60 minutes after addition was complete, 300 ml. of 20% aqueous sodium hydroxide solution was added and the reaction mixture was heated, with stirring, to 70° C. by heating in a water bath. The hydrocarbon layer was separated and washed successively with two 300 ml. portions of water.

The hydrocarbon layer was distilled to remove the unreacted xylene ethylbenzene, toluene and styrene. The yield of reaction products was 165 grams (158 wt. percent based on the styrene reactant). Upon distillation the following fractions were obtained:

No.	Wt. percent	Temp., ° C./ mm. Hg	N_D^{20}	D_4^{20}
1	46.7	295–302/745	1.5653	0.98
2	14.0	110–138/ 2	1.5700	0.99
3	30.2	188–245/ 2	1.5970	1.01
4	9.1	245/ 2	1.6070	(1)

[1] Solid.

Fraction 2 (50 pts.) comprising chiefly tricyclic hydrocarbons was hydrogenated in a 4-liter autoclave using 7 pts. Raney nickel catalyst and 500 ml. pentane as sol-

vent at 200° C. under 1300 p.s.i. hydrogen for 8 hours. After cooling and removing from the auto-clave the pentane solution was filtered and the pentane evaporated leaving a fluid in substantially quantitative yield, having a density (d_4^{20}) 0.94. It showed a heat of combustion of 19,500 B.t.u./lb. (gross), a net B.t.u./lb. of 18,255 and 143,119 net B.t.u./gallon.

Similarly, fraction 1, comprising dicyclic compound was hydrogenated to produce a fuel of 0.888 density and a heat of combustion (net) of 136,600 B.t.u./gallon.

EXAMPLE 2

Reaction of styrene with toleuene

The procedure of Example 1–A was followed to react 416 grams of styrene (4 moles) with 1656 grams (18 moles) of toluene. The BF_3— phenolate was replaced with 4 moles 97% H_2SO_4. The time of addition of the styrene was 2 hours an the temperature was maintained at 4±2° C. Stirring was continued for 2 hours at 4° C. after the styrene addition. A liter of ice water was added to the reaction mixture, the acid layer was removed, and the hydrocarbon layer was shaken with one liter of 3% sodium carbonate solution until no more carbon dioxide was released. The toluene was then removed by distillation at atmospheric pressure, and the remainder was distilled at 1 mm. Hg pressure. No unreacted styrene was found in the distillate. A yield of 169 wt. percent of products were obtained based on the styrene fed.

The product fractions collected in the distillation were as follows:

No.	Wt. percent	B.P. ° C./1 mm. Hg	N_D^{20}
1	3.0	124–129	1.5660
2	88.1	129–130	1.5670
3	2.4	130–132	1.5795
4	6.5	>132	1.5838

Fractions 1 and 2 were combined and properties of the composite were found to be as follows:

B.P., ° C. at 745 mm. Hg	279–285
d_4^{20}	0.982
M.P., ° C.	Below —50
Pour Point, ° C.	Below —50
Abs. viscosity, poises;	
At 0° C.	0.5
At —25° C.	0.5

Pentane (800 ml.) with 195 g. of the above composite and 30 g. of Raney nickel catalyst were charged to the hydrogenation autoclave and agitated under 1200 p.s.i. hydrogen for 7 hours at which time the pressure drop indicated complete hydrogenation. After removal of catalyst by filtration and evaporation of the pentane at 100° C., the following properties were obtained on the product (obtained in quantitative yield):

B.P., ° C./745 mm. Hg	275–281
N_D^{20}	1.4812
d_4^{20}	0.884
M.P., ° C.	Below —50
Pour point, ° C.	Below —50
Viscosity (poises):	
At 0° C.	0.5
At —25° C.	2.0
Heat of combustion:	
Gross B.t.u./lb.	19,610
Net B.t.u./lb.	18,342
Net B.t.u./gallon	135,236

In a second hydrogenation test, 30 g. of Raney cobalt catalyst genated fuel product was identical with that obtained with Raney nickel.

EXAMPLE 3

Reaction of styrene in effluent from ethylbenzene dehydrogenation

The reaction kettle of Example 1–A was employed to react a mixture (1991 g.) of hydrocarbons consisting of 738 g. styrene, 1219 g. ethylbenzene, 22 g. toluene and 12 g. benzene in the presence of an alkylation catalyst. This mixture simulates the effluent obtained in dehydrogenation of ethylbenzene in the manufacture of styrene. The total mixture was charged to the kettle immersed in a water bath. Sulfuric acid (203 g. of 96.9% acid) was added dropwise while stirring the kettle contents over a period of 5.25 hours. The rate of addition was regulated to maintain a temperature below 50° C. (After 10 minutes the acid addition was stopped while ice was added to the bath when the temperature exceeded 50° C.) Stirring was continued for 30 minutes after the acid addition was complete. The acid layer was separated and the hydrocarbon layer was washed successively with 1 liter 3% Na_2CO_3 solution, 1 liter water, and 1 liter water. Distillation to remove the unreacted hydrocarbons showed 105 wt. percent product yield (based on styrene). Distillation of the product gave the following fractions:

No.	Wt. percent	B.P. ° C. at 745 mm. Hg	N_D^{20}
1	3.3	175–250	1.5265
2	7.6	250–269	1.5474
3	21.7	269–270	1.5492
4	67.4	>270	(1)

[1] Decomposition began.

It appeared that decomposition of dimers of styrene was occurring giving styrene and other decomposition products after fraction 3 was collected. The distillation was stopped and a portion of fraction 4 (sample A, 208 grams) was removed for hydrogenation. Then fractions 1, 2, 3, and 4 were recombined in proper proportions to reconstitute the original product (sample B, 210 grams).

Samples A and B were hydrogenated separately with 30 g. each of Raney nickel catalyst and 800 ml. each of pentane under 1500 p.s.i. hydrogen pressure at 200 to 228° C. After filtering and evaporating the pentane, high energy fuels remained in essentially quantitative yield and having the following properties:

	Hydrogenated Sample A	Hydrogenated Sample B
B.P. ° C./745 mm. Hg	299–315	200–315
d_4^{20}	0.93	0.917
N_D^{20}	1.4982	1.4930
M.P., ° C	(1)	(2)

[1] 20 (glassy solid).
[2] Below —35° C.

Heat of Combustion	Hydrogenated Sample A	Hydrogenated Sample B
Gross B.t.u./lb	19,608	19,700
Net B.t.u./lb	18,335	18,425
Net B.t.u./gallon	142,205	140,950

EXAMPLE 4

Reaction of styrene in effluent from ethylbenzene dehydrogenation

Example 3 was repeated employing 1735 grams of the same hydrocarbon mixture and 203 g. of 96.9% sulfuric acid. In this run the reaction temperature was maintained under 25° C., and except for 5 minutes at near 25° C. the temperature was held at 5±2° C. The acid addition required 4.5 hours and stirring was continued thereafter for 1.75 hours. After washing as in Example 4 and distilla-

tion to remove unreacted hydrocarbons a product yield of 104% based on styrene was obtained. Distillation at 745 mm. mercury gave 21% distilling at 260 to 270° C. at which point decomposition commenced.

The distillation was discontinued and the residue and product distillate were recombined. Hydrogenation was conducted on a portion (200 g.) of this product, as for sample B of Example 3. The recovered hydrogenated fuel was substantially identical with the hydrogenated B product of Example 3, showing 141,100 net B.t.u./gallon, a slightly higher heating value.

Another portion of the alkylation product above was cooled to −20° C. and warmed up to 20° C. A crystalline fraction (about 50% of the total) was filtered off, it melted at 40 to 50° C. and comprised a crude mixture of styrene dimers. Hydrogenation of these dimers by the above process gave a product having a net energy of combustion of 18,350 B.t.u./lb. The filtrate from the dimers when similarly hydrogenated showed a net energy of combustion of 18,500 B.t.u./lb.

An alternative method of obtaining the hydrogenated dimers when such separate product is desired is that of hydrogenating the total product comprising dimers and alkylate, and separating the hydrodimers from the total hydrogenated product by a combination of fractional distillation and crystallization. However, it is preferred for convenience to separate the dimer fraction from the alkylation product and then to hydrogenate the dimers separately.

EXAMPLE 4–A

The hydrocarbon mixture employed in Example 3 (1991 g. containing 738 g. styrene) was added to a suspension of 404 g. 97% H_2SO_4 (4 moles) in 840 g. (7 moles) of ethylbenzene, while stirring, over a period of 3 hours. The temperature was maintained at 5±1° C. with an ice bath. After completion of addition and stirring for an additional hour at about 5° C., the reaction vessel contents were treated as in Example 3. A yield of 190% total product was obtained after removal of unreacted materials 95% of which distilled at 300 to 310° C. at 750 mm. mercury. Hydrogenation was conducted on the distillate over Raney cobalt catalyst (Girdler Company, #5362A T–323) under 1300 p.s.i. hydrogen at 150 to 200° C. in n-pentane for 6 hours. The pentane-free product separated therefrom had a density at 20° C. of 0.89 and showed a net B.t.u. per gallon of 136,850.

EXAMPLE 5

Reaction of styrene with ethylbenzene

The equipment of Example 1 was employed to react ethylbenzene with styrene. Fourteen moles (1484 g.) of ethylbenzene was charged to the reactor with 406 g. sulfuric acid (96.1%) and cooled to 40° C. in an ice water bath. Four moles of styrene (416 g.) was added dropwise, while stirring vigorously, over a period of 6.5 hours at a rate required to maintain 6±2° C. After styrene addition was completed stirring was continued one hour at 5° C. The acid layer was removed and the hydrocarbon product was washed once with 1 liter of 3% Na_2CO_3 solution and twice with a liter of water. The ethylbenzene was removed by distillation. The product amounting to 195 wt. % based on styrene were distilled at 745 mm. The fractions collected were as follows:

No.	Wt. percent	B.P. ° C./ 745 mm.	N_4^{20}	d_4^{20}
1	93.7	299–301	1.5592	0.972
2	1.0	307–309	1.5606	0.975
3	5.3	310	1.5757	0.98

The distillate (209 grams) was hydrogenated employing 31 g. of Raney nickel catalyst in 800 ml. pentane. The hydrogenation was conducted at 1250 p.s.i. hydrogen at a gradually increasing temperature over a 7-hour period from 150 to 230° C. After cooling, filtering and evaporating the pentane a substantially quantitative yield of hydrogenated fuel was obtained having the following properties:

B.P., ° C./746 mm.	296–306
N_D^{20}	1.4831
d_4^{20}	0.889
Melting point, ° C.	Below −50
Pour point, ° C.	Below −50
Viscosity (poises):	
At 0° C.	0.65
At −25° C.	2.25
Heat of combustion:	
Gross B.t.u./lb.	19,722
Net B.t.u./lb.	18,450
Net B.t.u./gal.	136,715

EXAMPLE 6

Reaction of styrene with synthetic xylenes

Example 5 was repeated substituting 16 moles (1700 g.) Sinclair synthetic xylenes (see Example 1–A for composition) for the 14 moles of ethylbenzene. The temperature during addition of the 4 moles of styrene was 7±3° C. and the time of addition was 4.75 hours. After all the styrene was added, the reaction mixture was heated to 35° C. while stirring for an hour. The separated and washed hydrocarbon layer was distilled to remove the unreacted hydrocarbons, and the yield of product was 190 wt. percent based on the styrene feed. Distillation gave the following fractions:

No.	Wt. percent	B.P. ° C/ 745 mm.	N_D^{20}
1	3.3	294–297	1.5602
2	59.7	297	1.5645
3	21.8	297–299	1.5660
4	15.2	< 299	1.5755

The combined distillate boiled at 294–299° C. and had a density d_4^{20} of 0.979 and a pour point of −35° C. A sample (209 g.) was hydrogenated according to the procedure of Example 5 under a maximum pressure of 1340 p.s.i. and a maximum temperature of 212° C. over a 6.5 hour period. The filtered and pentane-free product was obtained in quantitative yield. The following properties were measured:

B.P., ° C./745 mm.	285–290
N_D^{20}	1.4839
d_4^{20}	0.887
M.P., ° C.	Below −50
Pour point, ° C.	−48
Viscosity (poises):	
At 0° C.	0.5
At −25° C.	3.0
Heat of combustion:	
Gross B.t.u./lb.	19,725
Net B.t.u./lb.	18,452
Net B.t.u./gal.	136,545

EXAMPLE 7

Reaction of styrene and synthetic xylenes

Eaxmple 6 was repeated using BF_3 (0–1 mole) in 100 g. H_2SO_4 (97%). The total hydrocarbon product 185 wt. percent based on styrene feed) was hydrogenated. The final hydrogenated fuel was obtained in about 2% less overall yield (in comparison to Example 6) and the net heat of combustion was 137,000 B.t.u./gallon.

EXAMPLE 8

Reaction of styrene and benzene

The procedure of Example 5 was repeated employing 4 moles of styrene (416 g.), 18 moles benzene (1405 g.)

and 406 g. 96.1% sulfuric acid. The time of the styrene addition was 6.4 hours and the temperature of reaction was 6±1° C. Stirring was continued for 0.83 hrs. thereafter at 6° C. The product recovered as in Example 5, amounted to 149 wt. percent on the styrene feed (85.2% based on theoretical 100% alkylation of benzene by the styrene without styrene dimer formation). Distillation gave the following fractions:

No.	Wt. percent	B.P.° C. at 745 mm.	N_D^{20}
1	3.4	200–250	1.5129
2	3.3	250–269	1.5496
3	7.7	269	1.5685
4	18.9	269–271	1.5703
5	27.9	271–273	1.5714
6	38.8	>273	1.5845

Fractions 3, 4 and 5 combined showed the following properties:

B.P., ° C./745 mm.	269–273
N_D^{20}	1.5711
d_4^{20}	0.995
Pour point, ° C.	Below −50

A sample (181.3 g.) of this composite in 800 ml. pentane with 27 g. of Raney nickel catalyst was hydrogenated as in Example 5. The maximum pressure of hydrogen was 1250 p.s.i., hydrogenation commenced at about 130° C., and heating was continued for 5.25 hours up to a maximum temperature of 235° C. The cooled, filtered, solvent-free product (obtained by evaporation) was obtained in substantially quantitative yield. This hydrogenated fuel had the following properties:

B.P., ° C./745 mm.	265–270
N_D^{20}	1.4832
d_4^{20}	0.890
M.P., ° C.	Below −50
Pour point, ° C.	Below −50
Viscosity (poises):	
At 0° C.	0.50
At −25° C.	0.50
Heat of combustion:	
Gross B.t.u./lb.	19,795
Net B.t.u./lb.	18,535
Net B.t.u./gallon	137,530

Reaction of styrene and dedecylbenzene

The procedure of Example 5 was followed employing as reactants 2 moles styrene (208 g.) and 8 moles dodecylbenzene, and as catalyst 203 g. of 96.1% sulfuric acid. The time of addition of the styrene was 4.83 hours and the temperature during addition was 4±2° C. Stirring was continued at 4° C. for 0.75 hour thereafter. The total recovered product after washing and removing solvent was 70 wt. percent based on the styrene. It distilled above 190° C. at 7 mm. Hg pressure and had an N_D^{20} of 1.5462 and d_4^{20} of 0.961. The total product was hydrogenated with Raney nickel under 1100 p.s.i. hydrogen (as in Example 5) while increasing the temperature from 100 to 200° C. over a period of 4 hours. The yield of hydrogenated material was essentially quantitative:

N_D^{20}	1.4965
d_4^{20}	0.89
Heat of combustion:	
Gross B.t.u./lb.	19,077
Net B.t.u./lb.	17,800
Net B.t.u./gallon	132,200

EXAMPLE 10

Reaction of styrene and sec-amylbenzene

The procedure of Example 5 was employed to react styrene (4 moles) with sec-amylbenzene (12 moles) using 406 grams of 96.1% sulfuric acid. The styrene addition time was 4.75 hours and the temperature of addition was 6±1° C. Time of stirring after addition was complete was 1.75 hours. The washed and recovered product was 879 g. or 211 wt. percent of the styrene feed. Distillation gave the following fraction:

No.	Wt. percent	B.P.° C. at 745 mm.	N_D^{20}	d_4^{20}
1	1.3	322–326	1.5365	0.94
2	83.7	326–332	1.5453	0.952
3	4.8	332–335	1.5463	0.96
4	10.2	(1)	1.5705	

[1] Residue.

Hydrogenation of 251.4 g. was carried out using 37 g. of Raney nickel catalyst in 800 ml. pentane at 1025 p.s.i. hydrogen with agitation while heating from 100 to 200° C. over a period of 5 hours. The filtered solvent-free (by evaporation) product obtained in quantitative yield showed the following characteristics:

B.P., ° C./745	320–333
N_D^{20}	1.4860
d_4^{20}	0.890
Pour point, ° C.	−40
Melting point, ° C.	Below −50
Viscosity (poises):	
At 0° C.	2.0
At −25° C.	8.8
Heat of combustion:	
Gross B.t.u./lb.	19,610
Net B.t.u./lb.	18,330
Net B.t.u./gallon	136,010

EXAMPLE 11

Reaction of styrene and sec-butylbenzene

Example 10 was repeated employing 2 moles styrene (208 g.), 4.5 moles sec-butylbenzene (600 g.), and 203 g. of 96.1% sulfuric acid. The reaction temperature was 6±2° C. over the 2.75 hours of styrene addition. Stirring was continued 15 minutes before separation of the acid and washing. After removal of unreacted sec-butyl benzene a yield of 192% (by wt.) based on styrene feed was obtained. Distillation gave the following fractions:

No.	Wt. percent	B.P. ° C./ 745 mm.	N_D^{20}	d_4^{20}
1	5.1	310–16	1.5427	0.941
2	76.9	316–24	1.5509	0.959
3	18.0	(1)	1.5681	

[1] Residue.

Hydrogenation of 237 g. of the distillate was carried out with 800 ml. pentane and 35 g. Raney nickel under 1050 p.s.i. hydrogen while gradually increasing the temperature from 120 to 210° C. over a period of 4.5 hours.

The product recovered, in essentially quantitative yield showed the following characteristics:

B.P. ° C./745 mm.	307–321
N_D^{20}	1,4809
d_4^{20}	0.885
Viscosity (poises):	
At 0° C.	0.85
At −25° C.	3.0
Heat of combustion:	
Gross B.t.u./lb.	19,830
Net B.t.u./lb.	18,560
Net B.t.u./gallon	137,000

EXAMPLE 12

Reaction of styrene with cumene

The procedure of Example 10 was employed to react 2 moles of styrene (208 g.) with 7 moles cumene (840 g.) in the presence of 203 g. of 96.1% sulfuric acid. The

styrene was added over a period at 4.25 hours while maintaining a temperature of 5±1° C. Stirring was continued thereafter for 15 minutes at 4° C. Product obtained after removal of unreacted hydrocarbons was 186% by weight based on the styrene feed. Distillation at 745 mm. gave the following fractions:

No.	Wt. percent	B.P., ° C.	N_D^{20}	d_4^{20}
1	14.7	303–307	1.5511	0.96
2	74.9	307–310	1.5541	0.964
3	10.4	(1)	1.5640	

[1] Residue.

A part of fraction 2 (223 g.) was hydrogenated as in Example 1 using 33 g. of Raney nickel (Girdler G–49A) in 800 ml. pentane and 1000 p.s.i. hydrogen pressure. The temperature was gradually raised from 130 to 200° C. over a period of 5.5 hours. A substantially quantitative yield of hydrogenated fuel was recovered therefrom by the procedures of Example 1A. The characteristics of the fuel were:

B.P., ° C./745 mm.	303–309
N_D^{20}	1.4841
d_4^{20}	0.888
Pour point, ° C.	−42
Viscosity (poises):	
At 0° C.	0.85
At −25° C.	3.2
Heat of combustion:	
Gross B.t.u./lb.	19,494
Net B.t.u./lb.	18,221
Net B.t.u./gallon	134,835

EXAMPLE 13

Reaction of styrene with ethyltoluene

The procedure of Example 5 was employed substituting 14 moles of ethyltoluene for 14 moles of ethylbenzene. The styrene addition was extended over 4.5 hours maintaining a temperature of 4±2° C., and stirring was continued for 2 hours at 5° C. thereafter. The recovered product yield was 201 wt. percent on the styrene feed. Distillation at 745 mm. gave the following fractions:

No.	Wt. percent	B.P.,° C.	N_D^{20}
1	2.6	300–208	1.5558
2	83.9	208–314	1.5598
3	6.4	314–321	1.5604
4	7.1	(1)	1.5753

[1] Residue.

Fractions 1, 2 and 3 were combined and characterized as follows:

N_D^{20}=1.5600, d_4^{20}=0.972, pour point=−46° C.

Hydrogenation of 233 g. with 33 g. of Raney nickel catalyst was conducted under 1300 p.s.i. hydrogen while increasing the temperature from 150° C. to 240° C. over a 3-hour period. A 90% yield of hydrogenated fuel was obtained having the following properties:

B.P., ° C./745 mm.	295–305
N_D^{20}	1.4840
d_4^{20}	0.888
Pour point	−49
Viscosity (poises):	
At 0° C.	0.50
At −25° C.	3.2
Energy of combustion:	
Gross B.t.u./lb.	19,735
Net B.t.u./lb.	18,465
Net B.t.u./gallon	136,585

EXAMPLE 14

Reaction of alpha-methylstyrene with benzene

The procedure of Example 8 was employed to react 5 moles of alpha-methylstyrene (590 grams) with 15 moles of benzene (1170 g.) while agitating with 406 g. of sulfuric acid recovered from Example 5. The addition of the styrene derivative was extended over 5 hours at a temperature of 5±1° C. Stirring was continued 45 minutes thereafter at 7° C. The recovered product therefrom (as in Example 8) amounted to 58 wt. percent of the feed alpha-methylstyrene, 70.7% distilling at 299–304° C. at 745 mm. and having a density d_4^{20} of 0.99 and N_D^{20} of 1.5692. A portion of the distillate (150 g.) was combined with 22 g. of Raney nickel in 800 ml. pentane and was hydrogenated under 1275 p.s.i. hydrogen while the temperature was increased from 140° C. to 225° C. over a period of 5 hours. The recovered high energy fuel (150 g.) showed the following properties:

B.P., ° C./745 mm. Hg	315–320
N_D^{20}	1.5023
d_4^{20}	0.936
Pour point, ° C.	−26
Viscosity (poises):	
At 0° C.	2.0
At −25° C.	27.0
Energy of combustion:	
Gross B.t.u./lb.	19,650
Net B.t.u./lb.	18,385
Net B.t.u./gal.	143,405

EXAMPLE 15

Reaction of alpha-methylstyrene with toluene

The procedure of Example 2 was followed using 4 moles of alpha-methylstyrene acid were cooled to 2° C. and the methylstyrene was added at a rate to maintain 4° C. (±2° C.) over 4 hours addition time. After 1 hour additional stirring the product was recovered (5% by weight based on methylstyrene feed). Distillation gave 88.5% distilling at 131–132° C./1 mm. Hg with 11.5% residue. The distillate had an N_D^{20} of 1.5635, the residue (tricyclic) 1.5830. The density d_4^{20} of the distillate was 0.994. Part of the distillate (209 g.) was hydrogenated at 1250 p.s.i. hydrogen with 30 g. Raney nickel in 800 ml. pentane. A quantitative yield of product resulted after 40 hours hydrogenation at 120 to 225° C. The product had the following properties:

B.P., ° C./745 mm. Hg	315–318
N_D^{20}	1.5020
d_4^{20}	0.933
Pour point, ° C.	−29
M.P., ° C.	Below −50
Viscosity (poises):	
At 25° C.	0.5
At 0° C.	3.2
At −25° C.	6.2
Energy of combustion:	
Gross B.t.u./lb.	19,590
Net B.t.u./lb.	18,325
Net B.t.u./gal.	142,570

EXAMPLE 16

Reaction of alpha-methylstyrene with synthetic xylene

The procedure of Example 6 was followed substituting 4 moles of alpha-methylstyrene for the styrene of that example. The synthetic xylene and 306 g. of 96.1% sulfuric acid were cooled to 4° C. and the methylstyrene was added over a period of 5.6 hours maintaining a temperature of 5±1° C. After 0.9 hour additional stirring the hydrocarbon layer was washed and distilled to separate unreacted feed. The product amounted to 101 wt. percent of the methylstyrene feed. Distillation gave 89.2% by weight distilling at 301 to 305° C./745 mm. and having N_D^{20} of 1.5627 and d_4^{20} of 0.995.

Hydrogenation of the distillate (223 g.) was conducted with 33 g. of Raney nickel in 800 ml. pentane. In 5.5 hours at a maximum 1300 p.s.i. hydrogen the temperature was raised from 150° C. to 235° C. A yield of 90% of hydrogenated fuel was recovered therefrom.

B.P., ° C./745 mm.	312–320
N_D^{20}	1.5018
d_4^{20}	0.931
Pour point, ° C.	−27
M.P., ° C.	Below −50
Viscosity (poises):	
At 0° C.	3.0
At −25° C.	46.3
Energy of combustion:	
Gross B.t.u./lb.	19,580
Net B.t.u./lb.	18,310
Net B.t.u./gal.	142,155

EXAMPLE 17

Reaction of alpha-methylstyrene with ethylbenzene

Example 16 was repeated substituting 14 moles of ethylbenzene for the 16 moles of xylenes. The yield was 104 wt. percent on the methylstyrene feed, 3.5% distilling from 290 to 303° C. at 745 mm. Hg and 87.9% distilling at 303 to 308° C. (N_D^{20}=1.5622, d_4^{20}=0.985). A sample of the latter fraction of the distillate (223 g.) was hydrogenated quantitatively with 33 g. Raney nickel in 800 ml. pentane at 1350 p.s.i. hydrogen from 140° C. to 214° C. over a period of 5 hours. The hydrogenated fuel had the following properties:

B. P., ° C./745 mm.	310–316
N_D^{20}	1.5066
d_4^{20}	0.930
Pour point, ° C.	−29
Viscosities (poises):	
At 0° C.	4.0
At −25° C.	Below 50° C.
Energy of combustion:	
Gross B.t.u./lb.	19,510
Net B.t.u./lb.	18,240
Net B.t.u./gal.	142,085

EXAMPLE 18

Reaction of alpha-methylstyrene with cumene

The procedure of Example 4 was followed to react 3 moles of alpha-methylstyrene with 5 moles of cumene. One mole of 96.9% sulfuric acid (101.5 g.) was added dropwise to the hydrocarbon mixture over a period of one hour. Except for 2 minutes above 25° C. at the beginning the temperature was maintained at 12±6° C. during the addition of the acid. One hour additional stirring at 6° C. was given the reaction mixture. Washing of the hydrocarbon layer was effected by two washings with 1-liter each of 3% sodium carbonate solution and two water washes of 1-liter each. Distillation yielded 97 wt. percent product based on the methylstyrene feed. The following fractions were obtained:

No.	Wt. percent	B.P., ° C./745 mm.	N_D^{20}	d_4^{20}
1	2.2	250–301	1.5115	0.95
2	86.1	301–304	1.5637	0.99
3	11.7	(1)	1.5767	1.012

[1] Residue.

The residue comprised a tricyclic liquid product. Fraction 2 was hydrogenated with 15 g. of Raney nickel (per 100 g. of hydrocarbon) in 800 ml. of pentane solvent under 1300 p.s.i. hydrogen over 5 hours from 130 to 200° C. The hydrogenated fuel recovered in the described procedure (Example 4) showed almost quantitative yield with the following characteristics:

B.P., ° C./745 mm. Hg	312–317
N_D^{20}	1.5067
d_4^{20}	0.936
M.P., ° C.	Below −50
Pour point, ° C.	−50
Viscosity (poises):	
At 25° C.	0.5
At 0° C.	3.7
At −25° C.	148.0
Emergy of combustion:	
Gross B.t.u./lb.	19,550
Net B.t.u./lb.	18,350
Net B.t.u./gal.	143,130

The above hydrogenated product was found to be only 39% hydrogenated (based on carbon-hydrogen analysis). A second hydrogenation as above, but raising the final temperature to 240° C. and the hydrogen pressure to 1525 p.s.i. lowered the density (d_4^{20}) to 0.934 and increased the net heat of combustion to 18,465 B.t.u./lb. and 143,840 net B.t.u./gallon.

EXAMPLE 19

The procedure of Example 8 was employed to react 4 moles of vinyltoluene (472.7 g.) with 18 moles benzene (1405.5 g.) in the presence of 406 grams 96.1% sulfuric acid. The acid employed in this example was the acid recovered from Example 16. The addition of vinyltoluene to the acid benzene mixture required 3.6 hours to maintain a reaction temperature of 5±1° C. Stirring was continued for 0.75 hour. The hydrocarbon layer was washed free of acid and distilled giving a yield of 97 wt. percent (based on vinyltoluene) of product. The following benzene-free fractions were obtained.

No.	Wt. percent	B.P., ° C./745 mm.	N_D^{20}
1	6.7	225–284	1.5251
2	33.5	284–286	1.5432
3	2.2	[1] 286–280	[1] 1.5370
4	57.6	(2)	1.6063

[1] Decomposition commenced.
[2] Residue.

Reconstitution of sample of total product without residue was carried out by appropriate combination of the above 4 fractions, and 200 g. of such total product was hydrogenated in 600 ml. pentane using 30 g. of Raney nickel cobalt catalyst at 1500 p.s.i. hydrogen in 4 hours from 150 to 220° C.

A substantially quantitative yield of hydrogenated fuel was recovered therefrom having a pour point below −30° C., a density of 0.89 and net heats of combustion of 18,640 B.t.u./lb. and 138,000 B.t.u./gallon.

EXAMPLE 20

Reaction of vinyltoluene and toluene

The procedure of Example 2 was employed except that the 4 moles of styrene were replaced by 4 moles of vinyltoluene (472.7 g.). The recovered product yield was 135 wt. percent on the vinyltoluene feed. The distillation fractions obtained therefrom were as follows:

No.	Wt. percent	B.P., ° C./1 mm.	N_D^{20}
1	37.7	128–134	1.5608
2	20.3	134–138	1.5615
3	1.9	138–148	1.5655
4	1.0	148–164	1.5705
5	39.1	(1)	1.5807

[1] Residue.

The residue above was tricyclic in nature. The dicyclic distallate composite sample (fractions 1 thru 4) had a density (d_4^{20}) of 0.97 and a pour point of −50° C. Hydrogenation of the composite distillate (209.3 g.) using 32 g. of Raney nickel catalyst, 800 ml. pentane, 1300 p.s.i. hydrogen for 4 hours while increasing the temperature from 150° C. to 230° C. yielded quantitatively a high energy fuel having the following characteristics:

B.P., ° C./745 mm.	280–300
N_D^{20}	1.4810
d_4^{20}	0.883
Pour Point, ° C.	−49
Viscosity (poises):	
At 0° C.	0.5
At −25° C.	2.25
Energy of Combustion:	
Gross B.t.u./lb.	19,825
Net B.t.u./lb.	18,560
Net B.t.u./gallon	136,600

EXAMPLE 21

Reaction of vinyltoluene and synthetic xylenes

Example 6 was repeated except that the 4 moles of styrene therein were replaced by 4 moles of vinyltoluene (472 g.) and the two moles of acid were 96.8% in the present example instead of 96.1% sulfuric acid of Example 6. The yield was 170 wt. percent on the vinyltoluene feed and the following fractions were collected:

No.	Wt. percent	B.P., ° C./745 mm.	N_D^{20}
1	10.0	307–311	1.5592
2	70.0	311–312	1.5619
3	20.0	(1)	1.5773

[1] Residue.

Hydrogenation was conducted as in Example 6 but the final hydrogenation temperature was 240° C. in the present example. A quantitative yield of hydrogenated fuel resulted having the following characteristics:

B.P., ° C./744 mm.	293–299
N_D^{20}	1.4810
d_4^{20}	0.882
Pour point, ° C.	−35
M.P., ° C.	Below −50
Viscosity (poises):	
At 0° C.	0.65
At −25° C.	8.84
Heat of combustion:	
Gross B.t.u./lb.	19,765
Net B.t.u./lb.	18,505
Net B.t.u./gallon	136,105

EXAMPLE 22

Reaction of vinyltoluene and ethyltoluene

Example 13 was repeated except that 4 moles of vinyltoluene (472 g.) were used instead of 4 moles of styrene used in Example 13. The yield of alkylate plus dimers was 195 wt. percent based on the vinyltoluene feed indicating less than 5% dimer formation from the vinyltoluene. The fractions from distillation of this precursor product were as follows:

No.	Wt. percent	B.P., ° C./745 mm.	N_D^{20}
1	70.0	318–322	1.5573
2	12.5	322–324	1.5563
3	17.5	(1)	1.5705

[1] Residue.

The density of (d_4^{20}) of 1 and 2 combined was 0.963 and the pour point was −39° C. Hydrogenation of 237 g. of the distillate in the usual manner using 15 g. Raney cobalt per 100 g. of these precursor hydrocarbons gave substantially a quantitative yield of high energy fuel of the following characteristics:

B.P., ° C./745 mm.	309–316
N_D^{20}	1.4839
d_4^{20}	0.885
Pour point, ° C.	−45
M.P., ° C.	Below −50
Viscosity (poises):	
At 0° C.	0.85
At −25° C.	27.0
Heat of combustion:	
Gross B.t.u./lb.	19,800
Net B.t.u./lb.	18,535
Net B.t.u./gallon	136,790

EXAMPLE 23

Reaction of divinylbenzene and toluene

The procedure of Example 2 was employed to react 4 moles divinylbenzene (520 g.) with 16 moles toluene (1472 g.) in the presence of 4 moles of 95.8% sulfuric acid (408 g.). The divinylbenzene obtained from the Dow Chemical Co. had the following composition: 53 wt. percent divinylbenzene, 34.5 wt. percent ethyl vinylbenzene and 12.5 wt. percent saturated hydrocarbons chiefly diethylbenzene. The addition of the divinylbenzene required 7 hours to maintain the reaction temperature at 5±1° C. After the 15 minute period of additional stirring at 5° C. the acid layer was separated, the hydrocarbon layer was washed twice with 400 ml. portions of water and by 400 ml. of 5% Na_2CO_3 solution. Distillation to remove the unreacted toluene showed 173 wt. percent yield (based on divinylbenzene) of reaction product from which the following fractions were collected:

No.	Wt. percent	B.P., ° C./465 mm.	N_D^{20}	d^{20}_4
1	19.5	125–166	1.5550	0.964
2	9.9	166–205	1.5605	
3	28.0	205–225	1.5820	0.997
4	14.8	225–281	1.5840	
5	27.8	(1)	1.5930	

[1] Residue (solid).

A composite sample was prepared (150 g.) from fractions 1 and 2 above representing the dicyclic reaction products (Sample A) and a composite sample was prepared of the tricyclic distillate, i.e., fractions 3 and 4 which contained the tricyclic hydrocarbon precursor product (Sample B). The hydrogenation of Samples A and B were conducted as usual in preceding examples with 15 g. Raney nickel catalyst and 400 ml. pentane per 100 g. of precursor hydrocarbons. The hydrogen pressure was 1300 p.s.i. and the time was 5.5 hours from 150° C. to the 220° C. maximum temperature. The

hydrogenated products obtained essentially quantitatively therefrom were characterized as follows:

	Hydrogenated Sample A	Hydrogenated Sample B
B.P.,° C/45 mm	153–223	233–409
N_D^{20}	1.4831	1.5007
d_4^{20}	0.881	0.934
Pour Point, ° C	(1)	10
Viscosity at 0.° in poises	0.85	148.0
Heat of Combustion:		
Gross B.t.u./lb	19,710	19,545
Net B.t.u./lb	18,435	18,300
Net B.t.u./gallon	135,495	142,555

[1] Below −50.

It is apparent that the much higher density of the tricyclics results in the increased B.t.u./gallon values but when a low pour point is desired, it is preferred to have a blend of di- and tri-cyclic saturated compounds such as is obtained without separating the alkylate and dimer precursors into high boiling and low boiling fractions.

EXAMPLE 24

Reaction of divinylbenzene and ethylbenzene

Example 23 was repeated except that 14 moles of ethylbenzene were employed instead of 16 moles of toluene. The addition of the divinylbenzene was completed in 4.5 hours and the reaction temperature gradually increased from 4 to 12° C. during the reaction. After 30 minutes additional stirring, the hydrocarbon layer was separated and washed with 1 liter 3% sodium carbonate solution followed by two water washes of 1-liter each. The product (128 wt. percent on divinylbenzene feed) was distilled into 3 fractions as follows:

No.	Wt. percent	B.P.,° C./ mm. Hg	N_D^{20}
1	23.9	165/35 to 192/7	1.5470
2	32.1	192–300/7	1.5746
3	44	(1)	

[1] Residue (solid).

Hydrogenation of total distillate using the procedure of Example 23 gave a high energy fuel with the following properties:

B.P., ° C./7 mm.	150–285
N_D^{20}	1.4930
d_4^{20}	0.91
Pour point, °C.	Below −35
Heat of combustion: Net B.t.u./gallon	139,600

EXAMPLES 25 to 34

As mentioned hereinbefore, each catalyst system produces an ultimate product differing in amounts of the various isomers of hydrogenated alkylate and hydrodimers present. Also, the composition varies with conditions of alkylation. It has been further found that for each catalyst system there are preferred conditions of operation to attain optimum yields of precursors for hydrogenation to high energy fuels. When maximum alkylation and a minimum of dimer formation (including self-alkylation) is desired the preferred conditions for producing highest yields are shown in Table I, for a number of Lewis acids and Friedel-Crafts type catalysts. The ratio of vinylaromatic hydrocarbon to saturated aromatic compounds is always below 0.5 when alkylate is the desired major product.

TABLE 1

Example No.	Catalyst
25	Aluminum chloride/nitrobenzene (1/3 mole ratio).
26	Aluminum chloride/nitromethane (1/10 mole ratio).
27	Sulfuric acid (95–98%).
28	Ferric chloride.
29	Methane sulfonic acid/Boron fluoride (10/3 mole ratio,)
30	Aluminum chloride.
31	Aluminum chloride/carbon tetrachloride (1/1 mole ratio).
32	Hydrogen fluoride.
33	Aluminum chloride/Hydrogen chloride (1/1 mole ratio).
34	Hydrogen fluoride/Boron fluoride (100/1 mole ratio).

Preferred Conditions for the Alkylation of Aromatic Hydrocarbons (Formula II) with Vinylaromatic Hydrocarbons (Formula I) employing Lewis Acid or Friedel-Crafts Catalysts to Produce Optimum Yields of Precursors for the Fuels of the Present Invention (Formula II) compound exemplified, in Examples 1 to 10, by benzene, toluene, xylenes, ethylbenzene, cumene, ethyltoluene, butylbenzene, amylbenzene.

Example No.	Temp., ° C.	Molar Ratios		Total Hours of Reaction	Percent Dimer and Alkylated Dimer in Alkylate	Procedure [1]	Vinyl-aromatic Addition, Hours
		Catalyst/ Vinyl Group	Formula II/ Formula I				
25	20–25	0.4/1	4/1	1.5	15	A	0.3
26	20–25	1.0/1	5/1	1.5–2	15	A	0.3
27	0–5	0.5–1.0/1	3–5/1	1 to 2	5	A	1.0
28	−5–0	1/1	3–5/1	3	10	A	0.5
29	−25 to −20	0.5–0.6/1	3–5/1	1 to 2	25	A	1.0
30	−35 to −20	0.1/1	5/1	2 to 3	20	A	1.0
31	−40 to −30	0.2/1	5/1	2 to 3	30	A	1.0
32	−45 to −35	5/1	5/1	1.5–2	5	A	0.65
33	−70 to −50	0.2/1	5/1	2 to 3	25	A	0.5
34	−70 to −50	5/1	5/1	1.0 to 1.5	20	A	0.65

[1] Procedure A: Vinylaromatic hydrocarbon added gradually to aromatic hydrocarbon catalyst mixture while agitating vigorously and cooling the reaction flask in a cold bath (ice and salt water for 0° C. and above and Dry Ice-alcohol bath for 0 to −70° C.).

EXAMPLES 35 TO 46

Table II shows conditions preferred for increased dimer yields and decreased alkylate content of the reaction products.

Dimerization as opposed to alkylation becomes the major reaction product as the mole ratio of vinylaromatic compound (Formula I) to saturated aromatic compound (Formula II) is decreased below 2 and approaches 0.

In similar examples it was demonstrated that boron fluoride promoted with phenol (as the boron fluoride phenolate containing one or two moles phenol per mole of boron fluoride) can be used in place of the boron fluoride etherate, or boron fluoride methyl amine complexes, boron fluoride pyridine complexes and the like can be used as an alkylating catalyst under the conditions outlined in Tables I and II examples, in the process of the present invention. Likewise aluminum chloride promoted with water, alcohol, organic acid, a phenol, ether, ester, alkyl halide, a polyhalogenated methane, an amine, ethane, or propane (the promoter being used in a molar amount of 1 to 0.1 mole per mole of aluminum chloride) can be used as alkylating catalyst under the conditions exemplified in Tables I and II herein.

value, and have uses similar to those outlined for products in (A) above (e.g., Sample A of Example 3, Examples 4, 14, 15 and 35 to 46 inclusive).

In summarizing it is apparent that the fuels exemplified herein fall within the desired range of 130,000 to 145,000 B.t.u./gallon of fuel. Thus by the present invention novel liquid dicyclic high energy hydrocarbon fuels, the mixtures of cycloalkyl alkylcycloalkane derivatives including hydrogenated dimers of vinylaromatic hydrocarbons are provided wherein the alkane portion, or portions, contains from 1 to 18 carbon atoms and the total number of carbon atoms is in the range of 14 to 30. Also are provided solid di-cyclic and tricyclic hydrogenated fuels containing from 30 to 48 carbon atoms which in minor amounts may be retained in the liquid fuels, or may be separated for use as solid fuels. All such saturated products have other advantageous usages such as lubricants, plasticizers, dielectric oils, hydraulic fluids, power transmission fluids and the like.

The use of such new fuels in admixture with other high energy fuels is also visualized thus providing a means of enhancing the fuel value of presently used hydrocarbon fuels such as kerosene, dialkylcyclohexane, paramenthane and the like. Further they are valuable for admixing with

TABLE II

Example No.	Catalyst
35	93% H_2SO_4
36	89% H_2SO_4
37	80% H_2SO_4
38	70% H_2SO_4
39	BF_3 etherate
40	BF_3—H_3PO_4 (1/1)
41	$AlCl_3$
42	$FeCl_3$
43	HF (90%)
44	96% H_2SO_4
45	CH_3SO_3H—BF_3(10/1)
46	$SnCl_4$

Preferred Conditions for Producing a Preponderance of Dimers of Formula I Compounds in Alkylation Reactions with Formula II Compounds to produce Precursors for Hydrogenation to Products Useful as Plasticizers, Lubricants, and Like Products of the Present Invention (Molar Ratio of Formula II/Formula I Compounds from 2/1 to 0). Formula I Compounds exemplified in Runs 1 to 12 are styrene, vinyltoluene (o-, m-, p-), alpha C_1 to C_{12} alkylstyrene, propenylbenzene.

Example No.	Temp., ° C.	Molar ratios		Total Hours of Reaction	Percent Dimer or alkylated dimer in Product	Procedure [1]	Component Added (Hours Addition Time)
		Catalyst Vinyl Group	Formula II/ Formula I				
35	0-5	1/1	1/1	1	55	A	Formula I (0.5).
36	0-5	1/1	0 to 2	1	85	B	H_2SO_4 (0.5).
37	25-40	4/1	0 to 2	5	95	C	
38	25-40	4/1	0 to 2	8	95	C	
39	0-5	0.1/1	0 to 1	2	90	A	Formula I (0.5).
40	0-5	1/1	0 to 1	2	75	A	Do.
41	5-20	0.5-1/1	0 to 1	6	75	C	
42	20	0.5/1	0 to 1	6	75	A	Formula I (0.4).
43	−20 to 0	5/1	0.5	2	85	A	Formula I (0.6).
44	−20 to 0	1/1	0 to 2	2	90	B	H_2SO_4.
45	25	0.5	1/1	2	80	A	Formula I (1).
46	20	0.01/1	1/1	2	90	C	

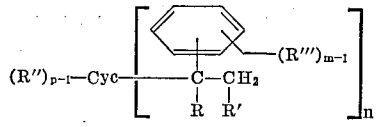
[1] Procedure A: (See Table I footnote).
Procedure B: Addition of the catalyst was gradually made to other ingredients of reaction mixture;
Procedure C: All components were added at start.

Thus by selective use of Friedel-Crafts and Lewis acids catalysts and conditions of operation either (A) high yields of alkylate isomeric (Formula III) compounds with minor amounts of dimers (Examples 25 to 34 inclusive) can be produced as precursors for hydrogenation, the products of which in the range of C_{14} to C_{30} molecules are useful as liquid fuels, lubricants, plasticizers for plastic materials, softeners and extenders, hydraulic fluids, dielectric fluids and the like, and in the range of greater than 30 carbon atoms are useful as solid fuels, greases, plasticizers, heat materials and the like, or (B) high yields of dimers with low yields of alkylate isomers (Formula III) are obtainable as precursors for hydrogenation and after hydrogenation these products also show high fuel boron hydride, the alkyl boron hydrides, the trialkyl borons, and the like, to minimize fire and toxicity hazards inherent with these boron derivatives per se.

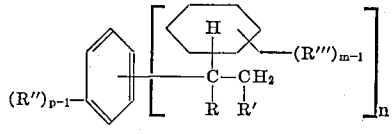
While there have been described herein what are at present considered preferred embodiments of the invention, it will be obvious to those skilled in the art that minor modifications and changes may be made without departing from the essence of the invention. It is therefore to be understood that the exemplary embodiments are illustrative and not restrictive to the invention, the scope of which is defined in the appended claims, and that all modifications that come within the meaning and range of equivalency of the claims are intended to be included therein.

I claim:

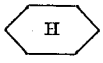
1. A composition of matter comprising a mixture of position isomers of at least one of Formula *a*:



and Formula *b*:

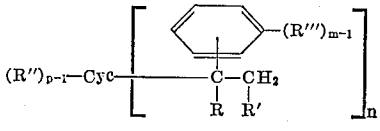


wherein in Formulas *a* and *b*



is a cyclohexane ring, R and R′ are members of the group consisting of hydrogen, alkyl, and Cyc-alkyl which together with the ethyl group contain 2 to 12 carbon atoms, R″ is a member of the group consisting of hydrogen, alkyl, and Cyc-alkyl, R‴ is a member of the group consisting of alkyl, Cyc-cycloalkyl, hexahydroindanyl and hexahydroalkindanyl, the hydrocarbon radicals R″ and R‴ each having from 1 to 12 carbon atoms, Cyc is a member of the group consisting of cyclo-C_5 and cyclo-C_6 alkanes, *m* is an integer of 1 to 5, *n* is an integer of 1 to 3 and *p* is an integer from 1 to 4.

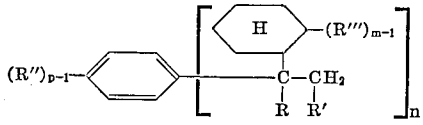
2. A composition of matter comprising a mixture of position isomers having the Formula *a*:



wherein R and R′ are members of the group consisting of hydrogen, alkyl, and Cyc-alkyl which together with the ethyl group contain 2 to 12 carbon atoms, R″ is a member of the group consisting of hydrogen, alkyl, and Cyc-alkyl, R‴ is a member of the group consisting of alkyl, Cyc-cycloalkyl, hexahydroindanyl and hexahydroalkindanyl, the hydrocarbon radicals R″ and R‴ each

having from 1 to 12 carbon atoms, Cyc is a member of the group consisting of cyclo-C_5 and cyclo-C_6 alkanes, *m* is an integer of 1 to 5, *n* is an integer of 1 to 3 and *p* is an integer from 1 to 4.

3. A composition of matter comprising a mixture of position isomers having the Formula *a*:



wherein R and R′ are members of the group consisting of hydrogen, alkyl, and Cyc-alkyl which together with the ethyl group contain 2 to 12 carbon atoms, R″ is a member of the group consisting of hydrogen, alkyl, and Cyc-alkyl, R‴ is a member of the group consisting of alkyl, Cyc-cycloalkyl, hexahydroindanyl and hexahydroalkindanyl, the hydrocarbon radicals R″ and R‴ each having from 1 to 12 carbon atoms, Cyc is a member of the group consisting of cyclo-C_5 and cyclo-C_6 alkanes, *m* is an integer of 1 to 5, *n* is an integer of 1 to 3 and *p* is an integer from 1 to 4.

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