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HYDROCARBON RADICALS

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This invention relates to a process for the preparation of hydrocarbons by coupling hydrocarbon radicals. More particularly, it relates to a thermal process for the production of coupled hydrocarbon radicals.

The pyrolysis of numerous types of hydrocarbons is well known including both aliphatic and aromatic hydrocarbons as well as alkaryl hydrocarbons. The products of the pyrolysis have normally been complex mixtures, sometimes including olefins, cracked degradation products and condensed products, from which certain compounds have been isolated. For example, petroleum alkyl aromatic hydrocarbons have been pyrolyzed at temperatures in the order of 700–1000° C. for the purpose of dealkylating the hydrocarbons, producing gaseous materials resulting from cleavage, and sometimes degradation of the alkyl radicals and the dealkylated cyclic hydrocarbon. Petroleum oils have also been pyrolyzed for the production of butadiene on the one hand and aromatic hydrocarbons on the other. The mixtures obtained by these processes are usually quite complex.

Heretofore, the coupling of hydrocarbon radicals has been achieved under certain limited conditions. For example, the Rust et al. patent, U.S. 2,755,322, shows the coupling of allylic groups to produce diallyl by heating allyl chloride in the presence of a promoter.

It is an object of the present invention to provide an improved process for the formation and coupling of hydrocarbon radicals. It is another object of this invention to provide a pyrolysis process for the production of coupled hydrocarbon radicals. It is a special object of the invention to provide a pyrolysis process for the coupling of hydrocarbon radicals wherein essentially no carbon or hydrogen is lost in the process to side reactions and wherein any residue of the starting material is recoverable for recycling. Other objects will become apparent from the following description of the invention.

Now, in accordance with the present invention, a process for the production of coupled hydrocarbons is provided by the pyrolysis of dihydroaromatic hydrocarbons bearing at least one hydrocarbyl radical directly attached to a saturated ring carbon atom. More particularly, the process of the invention comprises the pyrolysis of dihydro hydrocarbyl polycyclic hydrocarbons, especially wherein the hydrocarbon is a fused ring compound and wherein the hydrogen and aliphatic hydrocarbyl radicals are attached to a meso carbon atom, the pyrolysis conditions being such that the hydrocarbyl groups are pyrolyzed from the hydrocarbon and they couple to form dimers of hydrocarbyl radicals as neutral aliphatic hydrocarbons, the polycyclic aromatic compound being recovered separately. For the purpose of this disclosure, a meso carbon atom is defined as a nuclear carbon atom bonded to carbon atoms belonging to two different aromatic nuclei, as, for example, the two middle carbon atoms in anthracene (i.e., the 9- and 10-carbon atoms).

Still more particularly, optimum results are obtained by the pyrolysis at temperatures between about 350 and 550° C. of a dihydro tricyclic aliphatic hydrocarbyl hydrocarbon, especially a 9,10-dihydro-9,10-dialiphatic hydrocarbyl anthracene thereby producing a dimer of the hydrocarbyl group, which is recovered from the anthracene. An additional feature of the invention comprises the cyclic process in which the aromatic hydrocarbon recovered from the pyrolysis product is subjected to hydrogenation and alkylation (in either order) and then pyrolyzed again to recover coupled hydrocarbon products.

The hydrocarbons which may constitute the nucleus of the dihydro hydrocarbyl derivatives thereof are mono- and di-cyclic alicyclic or aromatic hydrocarbons, tricyclic aromatic hydrocarbons and tetra and higher cyclic aromatic hydrocarbons. They are represented by the following.

Mono- and di-cyclics:
- Benzene
- 1,3,5-cycloheptatriene
- Naphthalene

Tricyclic aromatics:
- Biphenylene
- Cyclopentaindene
- s-Indacene
- as-Indacene
- Pentathrene
- Acenaphthene
- Anthracene
- Phenanthrene
- Chrysene

Tetra- and higher cyclic aromatics:
- Benz-as-indacene
- 4,5-indenoindene
- 2,1-indenoindene
- 1,2-indenoindene
- 5,6-indenoindene
- Fluoranthene
- Aceanthrylene
- Naphthacene
- 1,2-benzanthracene
- Chrysene
- 3,4-benzophenanthrene
- Triphenylene
- Pentacene
- Picene
- Dibenzophenanthrene

The preferred materials for use in this process comprise anthracene, phenanthrene and acenaphthene. Tricyclic hydrocarbons which do not bear a fused ring may be utilized (such as phenylnaphthene) but the fused ring compounds are preferred. These tricyclic hydrocarbon nuclei may bear substituents other than those entering into the primary pyrolysis products but it is preferred that unsubstituted tricyclic aromatic hydrocarbons be employed. If, however, substituents other than those entering into the pyrolysis reaction are present, they may be aryl or alkyl substituents, such as phenyl, benzyl, ethyl or butyl groups or alkenyl radicals in positions not readily subject to splitting under the conditions employed. Substituents falling within these categories may be those listed hereinafter.

The dihydro polycyclic (preferably fused ring) aromatic hydrocarbons should bear at least one and preferably two hydrocarbyl substituents (which may be aliphatic, including substituted aliphatic such as an arylalkyl) each of which is attached to a saturated carbon atom of the dihydro aromatic hydrocarbon. Preferably, aliphatic hydrocarbon radicals have from 2 to 8 carbon atoms and still more preferably from 3 to 6 carbon atoms each. If the hydrocarbyl groups to be cleaved from the nucleus are aryl (including alkaryl, and aralkyl) radicals, they may contain 5–16 carbon atoms, preferably 6–12. They may be saturated aliphatic radicals or may contain unsaturated linkages which are preferably olefinic but may be acetylenic. From 0 to 3 unsaturated linkages may be present, preferably from 0 to 1. The most satisfactory unsaturated type of radical contains an allylic grouping. Suitable radicals for cleavage present in the alkyl dihydroaromatic precursor include alkyl (includes substituted alkyl such as

arylalkyl), alkenyl and aryl (includes substituted aryl such as alkaryl). Alkyl and alkenyl are meant to include both acyclic and cyclic. Representative alkyl radicals are: ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, isopropyl, isobutyl, tert-butyl, 2-ethylpropyl, 1-methylpropyl, benzyl, o-methylbenzyl, cyclopentyl and cyclohexyl. Typical alkenyl radicals which are useful are: propenyl (allyl), methallyl, 2-pentenyl, 2-methyl-2-butenyl, 3-pentenyl, 4-pentenyl, 2-butenyl, 3-butenyl, 2,3-dimethyl-2-butenyl, 1,1-dimethyl-2-propenyl, 1-methyl-2-propenyl and cyclopent-2-enyl.

Aryl substituents may include the following.

Aryl radicals:

Benzyl
Phenyl
Naphthyl
Biphenyl
Tolyl
Xylyl
o-Methylbenzyl

Representative aryl radicals are: phenyl, alpha-naphthyl, beta-naphthyl, biphenyl, tolyl and xylyl.

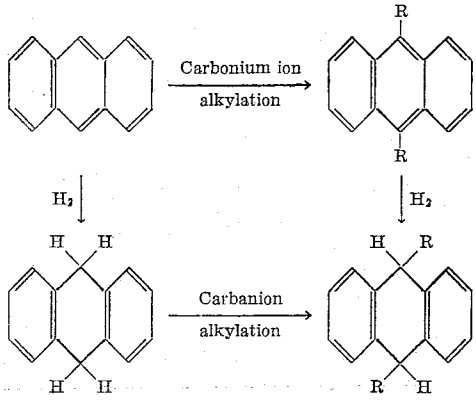
As noted above, the dihydro aromatic hydrocarbons should bear at least 1 aliphatic hydrocarbyl substituent attached to a saturated carbon atom. If two or more such substituents are attached to the dihydro aromatic, they are preferably attached to different saturated carbon atoms. If more than 1 aliphatic hydrocarbyl radical is present in a single molecule, then the several radicals may be the same or different as desired, the choice in this respect being the identity of the desired coupled hydrocarbon product(s).

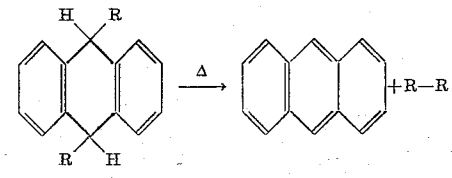
The following list of aliphatic hydrocarbyl aromatic hydrocarbons illustrates the type of materials which are particularly suitable for use in the described pyrolysis process. While the dihydro dihydrocarbyl derivatives are so listed, it will be understood that comparable and suitable derivatives include those having from 1 to about 4 hydrocarbyl substituents attached to saturated carbon atoms.

Hydrocarbyl hydroaromatic hydrocarbons:

9,10-dihydro-9,10-diisopropylanthracene
9,10-dihydro-9,10-diallylanthracene
9,10-dihydro-9-allyl-10-isopropyl anthracene
9,10-dihydro-9-isopropyl-10-tert-butyl anthracene
9,10-dihydro-9,10-diisopropylacenaphthene
9,10-dihydro-9,10-di-tert-butyl acenaphthene
9,10-dihydro-9,10-dimethallyl acenaphthene
9,10-dihydro-9,10-di(2-methylbutyl)phenanthrene
9,10-dihydro-9,10-di(2-pentenyl)phenanthrene
9,10-dihydro-9,10-diallylphenanthrene
1,4-dihydro-1,4-dibenzylbenzene
1,4-dihydro-1,4-diphenylnaphthalene
5,6-dihydro-5,6-divinylnaphthacene
5,6,7-trihydro-5,6,7-tripropylpentacene

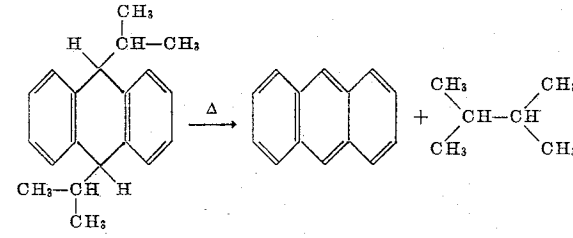
The principal reactions upon which this invention is based are as follows, the anthracene nucleus being utilized only for illustrative purposes.





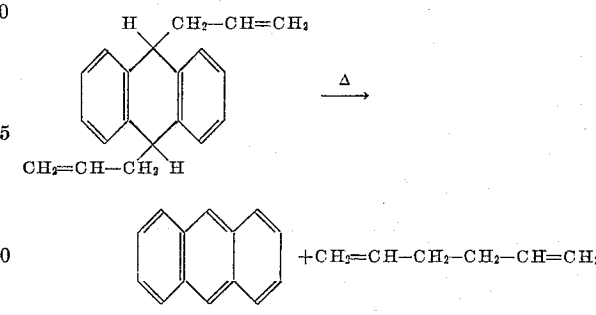
It will be noted from the above diagram of the reaction involved that the hydrocarbyl hydroaromatic compound may be formed by at least two alternative routes, one in which a hydrogen atom is replaced by the hydrocarbyl constituent, after which hydrogenation is employed to provide the additional hydrogen required as described hereinbefore. Alternatively, the tricyclic aromatic hydrocarbon may be first hydrogenated and then subjected to alkylation (as more fully described hereinafter) to provide the hydrocarbyl hydroaromatic hydrocarbon. The latter compound is then subjected to pyrolysis to produce a coupled product of two of the hydrocarbyl constituents and the original aromatic hydrocarbon. The latter may then be recycled to the first step for the production of the hydrocarbyl hydroaromatic hydrocarbon which is then subjected to a second cycle of the pyrolysis treatment.

In order to more fully illustrate and explain specific examples of the process before describing the latter, the following details are presented:



In the above reaction the 9,10-dihydro-9,10-diisopropylanthracene is pyrolyzed to produce 2,3-dimethylbutane and anthracene.

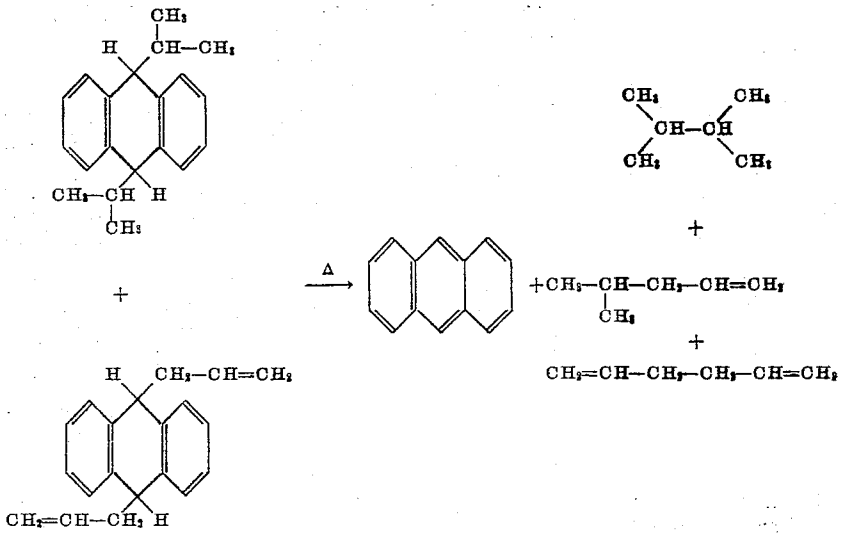
The pyrolysis of 9,10-dihydro-9,10-diallylanthracene is illustrative of the pyrolysis of a compound containing an unsaturated substituent.



It will be seen from the above course of reaction that the two principal products thereof are anthracene and 1,5-hexadiene.

Similarly, 9,10-dibenzyl-9,10-dihydroanthracene, upon pyrolysis, yields dibenzyl and anthracene.

While a single aromatic nucleus may contain more than one type of hydrocarbyl constituent in order to obtain desired products, it may be preferable to utilize a mixture of starting material (rather than mixed starting materials) if such products are desired. The following reaction illustrates this aspect.



According to the above reaction, a mixture of diisopropyl and of diallyl dihydro anthracenes is pyrolyzed to produce anthracene and a mixture of coupled hydrocarbyl products. The latter are three principal constituents, namely, 2,3-dimethyl butane (resulting from the coupling of two isopropyl radicals), 4-methyl-1-pentene (resulting from the coupling of an allyl radical and an isopropyl radical) and 1,5-hexadiene (diallyl). It will be seen, therefore, that the starting materials may be chosen to produce a precisely defined coupled product or a mixture of coupled products.

The pyrolysis step itself is relatively simple, the starting materials such as those described above being passed through a pyrolysis tube at an elevated temperature between about 350 and 550° C., preferably between about 400 and 500° C., the residence at such temperature being a time between about 1 and 120 seconds, preferably between about 15 and 60 seconds, dependent upon the temperature and the identity of the compound or compounds being pyrolyzed. The pyrolysis may be conducted in the presence of relatively inert substances (such as nitrogen, helium, flue gas or carbon monoxide) although the latter are not essential. The pyrolysis may be carried out under a variety of pressure conditions, atmospheric pressure being preferred for its convenience. However, reduced or increased pressure may be employed, the pressures varying from about 1 millimeter of mercury to as much as 1000 atmospheres. The products may be separated in a packed or unpacked fractionating column or heated pipe or vessel by known means to recover the coupled product and the precursor aromatic hydrocarbon. The aromatic is then utilized for the production of further quantities of the hydrocarbyl hydroaromatic compounds to be employed in the pyrolysis step.

The hydrogenation and alkylation steps per se may be carried out according to known processes. For example, the alkylation of a dihydroaromatic hydrocarbon may be conducted by means of heating a dihydroaromatic hydrocarbon with an olefin in the presence of a catalyst such as an alkali metal, mixtures thereof or mixtures of an alkali metal with other promoters such as iron. The conditions for such catalytic alkylation processes vary from about 0 to about 500° C. and may be conducted preferably under high pressure from about 5 to about 3000 atmospheres, the time of alkylation being from about 10 minutes to about 8 hours. Suitable processes are described in greater detail in Woodman patent, U.S. 2,448,641; Little, U.S. 2,548,803; Field, U.S. 2,823,240. The Pines Patent U.S. 2,670,390 also describes suitable alkylation procedures.

In addition to the carbanion reactions upon which the alkylation processes described in these patents depend, alkylation by means of a carbonium ion may be employed of which the Friedel Crafts reaction is typical. In such reactions an aromatic hydrocarbon is treated with an olefin or halogenated hydrocarbon preferably in the presence of a Friedel Crafts catalyst which may be boron fluoride-hydrogen fluoride, aluminum chloride-hydrogen chloride or other well known Friedel Crafts catalysts. The products of these alkylations may be fractionated prior to use if necessary or desired. The conditions for Friedel Crafts reactions and similar alkylation processes are known but preferably include the use of a catalyst in an amount from about 1% to about 10% by weight of the aromatic compound, the olefin being added gradually while the temperature is maintained between about 10 and 100° C., preferably between about 25 and 75° C. HCl may be added as an activator for the catalyst.

As mentioned hereinbefore, the product to be pyrolyzed must be hydrogenated prior to or subsequent to alkylation to an extent such that the carbon atoms to which the hydrocarbyl radicals are attached are saturated. Hydrogenation may be carried out, for example, by utilizing the conditions described in U.S. Patent 2,373,501 to Peterson or U.S. 2,391,283 to Weber et al. The conditions include contacting the compound and at least a stoichiometric amount of hydrogen at temperatures in the range from room temperature to about 350° C. with a catalyst prepared, for example, by leaching a nickel-aluminum alloy (Raney nickel) with a cold sodium hydroxide solution followed by consecutive displacement with cold water, methanol and hydrocarbon.

The pyrolysis process of this invention is preferably conducted with the use of tricyclic aromatics as the nucleus since, when utilizing aromatics having one or two aromatic rings, some side reactions occur, such as disproportionation.

The following examples illustrate the process of this invention. Anthracene was treated first with sodium in ethyl ether and then with isopropyl iodide or allyl bromide to produce the two starting materials used in Examples I–III by the following methods.

EXAMPLES I, II AND III

A benzene solution of each of the two materials prepared as described above was heated at a temperature of about 450° C. and the volatile products passed through a quartz tube for a residence time of approximaetly 24 seconds. Table I below outlines the products obtained by this process.

Table I

PYROLYSIS OF 9,10-DIHYDROANTHRACENE DERIVATIVES

Example	I	II	III
Percent w. in Benzene:			
9,10-dihydro-9,10-diisopropyl anthracene	20	------	10
9,10-dihydro-9,10-diallyl anthracene	------	20	10
Products (moles/100 moles 9,10 compounds fed):			
2,3-dimethylbutane	36	------	3
1,5-hexadiene	------	35	7
4-methyl-1-pentene	------	------	12
Propylene	15	5	19
Propane	29	2	32
Benzene recovered (Percent)	63	68	73
Conversion of 9.10 (Percent)[a]	83	60	64
Selectivity for coupling (Percent)[b]:			
9,10-diisopropyl	44	------	28
9,10-diallyl	------	58	40

[a] Estimated from solid recovery.
[b] Does not include benzene.

EXAMPLE IV

When 9,10-dihydro-9,10-dimethallyl phenanthrene is pyrolyzed at 400° C. using a residence time of about 40 seconds, the principal products are phenanthrene and 2,5-dimethyl-1,5-hexadiene.

EXAMPLE V

When the same pyrolysis conditions are employed for the pyrolysis of 9,10-dihydro-9,10-di-tert-butyl phenanthrene, the principal products ane phenanthrene and 2,2,3,3-tetramethyl butane.

EXAMPLE VI

When the same pyrolysis conditions are employed, using a mixture of the two phenanthrene derivatives employed in Examples IV and V, the three principal products obtained in addition to phenanthrene are 2,5-dimethyl-1,5-hexadiene, 2,2,3,3-tetramethyl butane and 2,4,4-trimethylpentene-1.

EXAMPLE VII

If 1,2-dihydro-1-allyl-2-isopropyl acenaphthene is pyrolyzed at 500° C. using a residence time of about 15 seconds, the principal products in addition to acenaphthene are 2,3-dimethyl butane, 1,5-hexadiene and 4-methyl pentene-1.

EXAMPLE VIII

When 9,10-dihydro-9-isopropyl anthracene is pyrolyzed at 375° C. for about 1 minute residence time, the principal product in addition to anthracene is 2,3-dimethylbutane.

EXAMPLE XI

Under the same conditions of pyrolysis, 9,10-dihydro-9-methallyl anthracene yields 2,5-dimethyl-1,5-hexadiene and anthracene.

EXAMPLE X

The pyrolysis of a mixture of the anthracene derivatives utilized in Examples VIII and IX includes as principal products the two end products described in those examples and in addition thereto 2,4-dimethyl-pentene-1.

EXAMPLE XI

The pyrolysis of a mixture of 9,10-dihydro-9,10-diisopropyl anthracene and 9,10-dihydro-9,10-di-tert-butyl-anthracene at about 500° C. results in the production of 2,3-dimethyl butane, 2,2,3,3-tetramethyl butane and 2,2,3-trimethyl butane.

EXAMPLE XII

Pyrolysis of a mixture of 9,10-dihydro-9,10-diallyl anthracene and 9,10-dihydro-9,10-dimethallyl anthracene at 525° C. yields 1,5-hexadiene, 2,5-dimethyl-1,5-hexadiene and 2-methyl-1,5-hexadiene.

We claim as our invention:

1. A process for preparing diisopropyl which comprises pyrolyzing 9,10-dihydro-9,10-diisopropylanthracene at a temperature of about 450° C. and recovering diisopropyl and anthracene.

2. A process for preparing diallyl which comprises pyrolyzing 9,10-dihydro-9,10-diallyl anthracene at a temperature of about 450° C. and recovering diallyl and anthracene.

3. A process for preparing a dialkyl which comprises pyrolyzing a 9,10-dihydro-9,10-dialkyl anthracene at a temperature between about 350 and 550° C. and recovering anthracene and a corresponding dialkyl.

4. A process for preparing a dialkenyl which comprises pyrolyzing a 9,10-dihydro-9,10-dialkenylanthracene at a temperature between about 350 and 550° C. and recovering anthracene and a corresponding dialkenyl.

5. A process for preparing a dimer of an aliphatic hydrocarbon radical which comprises pyrolyzing a 9,10-dihydro-9,10-di(aliphatic hydrocarbyl)anthracene at a temperature between about 350 and 550° C. and recovering anthracene and a corresponding aliphatic dihydrocarbyl.

6. A process for preparing a dimer of aliphatic hydrocarbon radicals which comprises pyrolyzing a dihydro di-(aliphatic hydrocarbyl) derivative of a fused-ring tricyclic aromatic hydrocarbon wherein the hydrocarbyl radicals are directly attached to saturated nuclear carbon atoms at a temperature between about 350° C. and 550° C. and recovering a corresponding tricyclic aromatic hydrocarbon and a corresponding aliphatic dihydrocarbyl.

7. A process for preparing a dimer of aliphatic hydrocarbon radicals which comprises pyrolyzing a dihydro di-hydrocarbyl derivative of a fused-ring polycyclic aromatic hydrocarbon consisting at least in part in an anthracene nucleus, wherein the hydrocarbyl groups are directly attached to meso carbon atoms at a temperature between about 350° C. and about 550° C. and recovering a fused ring polycylic aromatic hydrocarbon and a dihydrocarbyl.

8. A process according to claim 7 wherein the hydrocarbyl groups are alkyl radicals having 2–6 carbon atoms each.

9. A process according to claim 7 wherein the hydrocarbyl groups are 2-alkenyl radicals having 3–6 carbon atoms each.

10. A cyclic process for the preparation of diisopropyl which comprises pyrolyzing 9,10-dihydro-9,10-diisopropyl-anthracene at a temperature between about 350 and 550° C., separately recovering anthracene and diisopropyl, isopropylating and hydrogenating the recovered anthracene, whereby 9,10-dihydro-9,10-diisopropyl anthracene is prepared, and recycling it to the pyrolysis step.

11. A process for preparing a dimer of aliphatic hydrocarbon radicals which comprises pyrolyzing a dihydro-hydrocarbyl derivative of a fused ring polycyclic aromatic hydrocarbon containing at least one saturated ring carbon atom having an aliphatic hydrocarbyl radical directly attached thereto at a temperature between about 350 and 550° C. and recovering a fused ring polycyclic aromatic hydrocarbon and a corresponding aliphatic dihydrocarbyl.

12. A process according to claim 11 wherein the recovered polycyclic aromatic hydrocarbon is hydrogenated and hydrocarbylated, whereby a dihydrohydrocarbyl derivative of the fused ring polycyclic hydrocarbon is formed in which the hydrocarbyl groups are directly attached to saturated ring carbon atoms and recycling the hydrocarbylated and hydrogenated product to the pyrolysis step.

No references cited.