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(71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US).

(72) Inventor: SO, Ying-Hung ; 1524 Dilloway Drive, Midland, MI 48640 (US).

(74) Agent: RUSSELL, H., David; The Dow Chemical Company, P.O. Box 1967, Midland, MI 48641-1967 (US).

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**(54) Title:** A PROCESS FOR THE PREPARATION OF CYCLOBUTENE-SUBSTITUTED AROMATIC HYDROCARBONS

**(57) Abstract**

Process for the preparation of an aromatic hydrocarbon with a cyclobutene ring fused to the aromatic hydrocarbon which comprises, dissolving an ortho-alkyl halomethyl aromatic hydrocarbon in an inert solvent and pyrolyzing the solution of ortho-alkyl halomethyl aromatic hydrocarbon in the inert solvent under conditions such that the ortho-alkyl and the halomethyl substituents form a cyclobutene ring thereby forming an aromatic hydrocarbon having a fused cyclobutene ring. The ortho-alkyl group has the structural formula $(R')_2$-CH-, wherein R′ is separately in each occurance hydrogen or a $C_{1-20}$ alkyl. The aromatic hydrocarbons with a cyclobutene ring fused to the aromatic hydrocarbon are useful in the preparation of monomers, which are then useful in the preparation of high performance polymers.

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# A PROCESS FOR THE PREPARATION OF CYCLOBUTENE-SUBSTITUTED AROMATIC HYDROCARBONS

This invention relates to a process for the preparation of aromatic hydrocarbons with cyclobutene rings fused thereto.

Aromatic hydrocarbons with cyclobutene rings fused thereto are useful in the preparation of monomers, which are useful in the preparation of high performance polymers. These high performance polymers are useful as films, moldable compositions, adhesives, and in the preparation of composites.

Processes for the preparation of aromatic hydrocarbons with cyclobutene rings fused thereto suffer from two major problems. The first problem is that such synthesis involves complex multi-step sequences. Furthermore, some processes result in low yields of the desired product.

What is needed is a process for the preparation of cyclobutene-substituted aromatic hydrocarbons which is simple and results in high yields of said hydrocarbons.

The invention is a process for the preparation of an aromatic hydrocarbon with a cyclobutene ring fused to the aromatic hydrocarbon which comprises, dissolving an ortho alkyl halomethyl aromatic hydrocarbon in an inert solvent and pyrolyzing the solution of ortho-alkyl halomethyl aromatic hydrocarbon in the inert solvent under conditions such that the ortho-alkyl and the halomethyl substituents form a cyclobutene ring thereby forming an aromatic hydrocarbon having a fused cyclobutene ring. The ortho-alkyl group having the structural formula $(R')_2$-CH-, where R' is separately in each occurance hydrogen or a $C_{1-20}$ alkyl, preferably hydrogen or $C_{1-3}$ alkyl, and most preferably hydrogen.

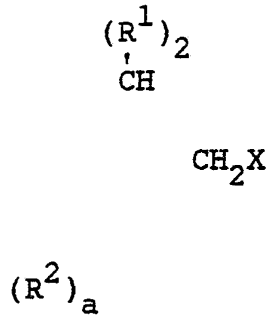
This process results in a one-step preparation of cyclobutene-substituted aromatic hydrocarbons in which the hydrocarbons are prepared in high yields.

The starting materials for this process include any aromatic hydrocarbon which has a $(R')_3$-CH- alkyl group and a halomethyl group ortho to one another. Preferred aromatic hydrocarbons include benzene, naphthalene, phenanthracene, anthracene, biphenyl, binaphthyl, or a diaryl alkane. More preferred aromatic hydrocarbons include benzene, naphthalene, biphenyl, binaphthyl, or a diphenylalkane. The most preferred aromatic hydrocarbon is benzene.

The R' substituent of the $(R')_2$-CH- group is preferably hydrogen or a $C_{1-3}$ alkyl and more preferably hydrogen. The halomethyl hydrocarbon is preferably bromomethyl or chloromethyl.

The aromatic hydrocarbon can be further substituted with one or more of the following substituents: a carbonyloxyhydrocarbyl, oxycarbonylhydrocarbyl, carboxyamide, carboxy, carbonylhalo, cyano, nitro, hydroxy, hydrocarbyloxy, or halo group. It is preferable that the aromatic hydrocarbon be substituted with one or more of such substituents. Preferred substituents are carbonyloxyhydrocarbyl, oxycarbonylhydrocarbyl, carboxamide, carboxy, carbonylhalo, nitro, or hydrocarbyloxy. More preferred substituents are carbonyloxyhydrocarbyl, oxycarbonylhydrocarbyl, carboxamide or oxyhydrocarbyl. Even more preferred substituents are the carbonyloxyalkyl hydrocarbons with carbonyloxymethyl being most preferred.

In one preferred embodiment wherein the aromatic hydrocarbon is benzene the starting materials correspond to the following formula



wherein

$R^1$ is separately in each occurrence hydrogen or $C_{1-20}$ alkyl; and

$R^2$ is separately in each occurrence carbonyloxyhydrocarbyl, oxycarbonylhydrocarbyl, carboxamide, carboxylate, carbonylhalo, cyano, nitro, hydroxy, hydrocarbyloxy or halo;

X is chloro or bromo; and

a is an integer of between 0 and 4 inclusive.

Examples of preferred starting reactants include: ortho-methylchloromethylbenzene, ortho-ethylchloromethylbenzene, ortho-propylchloromethylbenzene, ortho--butylchloromethylbenzene, ortho-pentylchloromethylbenzene, ortho-hexylchloromethylbenzene, 3- or 4-methoxy ortho-methylchloromethylbenzene, 3- or 4-methoxy ortho-ethylchloromethylbenzene, 3- or 4-methoxy ortho-propylchloromethylbenzene, 3- or 4-methoxy ortho-butylchloromethylbenzene, 3- or 4-ethoxy ortho-methylchloromethylbenzene, 3- or 4-ethoxy ortho-ethylchloromethylbenzene, 3- or 4-ethoxy ortho-propylchloromethylbenzene, 3- or 4-ethoxy ortho-butylchloromethylbenzene, 3- or 4-propoxy ortho-methylchloromethylbenzene, 3- or 4-propoxy ortho--ethylchloromethylbenzene, 3- or 4-propoxy ortho--propylchloromethylbenzene, 3- or 4-propoxy ortho-butylchloromethylbenzene, 3- or 4-butoxy ortho-methylchloromethylbenzene, 3- or 4-butoxy ortho-ethylchloromethylbenzene, 3- or 4-butoxy ortho-propylchloromethylbenzene, 3- or 4-butoxy ortho-butylchloromethylbenzene, 3- or 4-pentoxy ortho-methylchloromethylbenzene, 3- or 4-pentoxy ortho-ethylchloromethylbenzene, 3- or 4-pentoxy ortho-propylchloromethylbenzene, 3- or 4-hexoxy ortho-methylchloromethylbenzene, 3- or 4-hexoxy ortho-ethyl-chloromethylbenzene, 3- or 4-hexoxy ortho-propylchloro-methylbenzene, 3- or 4-hexoxy ortho-butylchloromethyl-benzene, methyl 3,4-ortho-methylchloromethylbenzoate, methyl 3,4-ortho-ethylchloromethylbenzoate, methyl 3,4-ortho-propylchloromethylbenzoate, methyl 3,4-ortho-butylchloromethylbenzoate, ethyl 3,4-ortho-methylchlo-romethylbenzoate, ethyl 3,4-ortho-ethylchloromethylben-zoate, ethyl 3,4-ortho-propylchloromethylbenzoate, ethyl 3,4-ortho-butylchloromethylbenzoate, propyl 3,4-ortho-methylchloromethylbenzoate, propyl 3,4-ortho-ethylchlo-romethylbenzoate, propyl 3,4-ortho-propylchloromethyl-benzoate, propyl 3,4-ortho-butylchloromethylbenzoate, butyl 3,4-ortho-methylchloromethylbenzoate, butyl 3,4-ortho-ethylchloromethylbenzoate, butyl 3,4-ortho-pro-pylchloromethylbenzoate, butyl 3,4-ortho-butylchloro-methylbenzoate, pentyl 3,4-ortho-methylchloromethylben-zoate, pentyl 3,4-ortho-ethylchloromethylbenzoate, pentyl 3,4-ortho-propylchloromethylbenzoate, pentyl 3,4-ortho--butylchloromethylbenzoate, hexyl 3,4-ortho--methylchloromethylbenzoate, hexyl 3,4-ortho-ethylchloro-methylbenzoate, hexyl 3,4-ortho-propylchloromethylbenzoate, hexyl 3,4-ortho-butylchloromethylbenzoate, benzyl 3,4-ortho-methylchloromethylbenzoate, benzyl 3,4-ortho--ethylchloromethylbenzoate, benzyl 3,4-ortho-propylchloro-methylbenzoate, benzyl 3,4-ortho-butylchloromethylbenzo-ate, phenyl 3,4-ortho-methylchloromethylbenzoate, phenyl 3,4-ortho-ethylchloromethylbenzoate, phenyl 3,4-ortho-propylchloromethylbenzoate, and phenyl 3,4-ortho-butyl-chloromethylbenzoate. For the preferred starting reactants, the butyl groups are selected from normal, iso or secondary butyl groups, but not tertiary butyl groups.

In one even more preferred embodiment, the starting material is methyl 3,4-ortho-methylchloromethylbenzoate.

The product prepared by the process of this invention is an aromatic hydrocarbon with a cyclobutene ring fused to one of the rings of the aromatic hydrocarbon. The preferred aromatic hydrocarbons are described hereinbefore. The product can be substituted as described hereinbefore.

In one preferred embodiment, wherein the aromatic hydrocarbon is benzene the products correspond generally to the formula

$(R^1)_2$

$(R^2)_a$

wherein $R^1$, $R^2$ and a are as defined hereinbefore.

Among preferred classes of aromatic hydrocarbons with cyclobutene rings fused thereto include cyclobutabenzene (bicyclo(4.2.0)octa-1,3,5,7-tetraene) 1-alkylcyclobutabenzenes, hydrocarbyl cyclobutabenzoate, hydrocarbyl 1-alkylcyclobutabenzoate, hydrocarboxy cyclobutabenzene, hydrocarboxy 1-alkylcyclobutabenzene, cyclobutabenzamides, and 1-alkylcyclobutabenzamides. Even more preferred classes include alkyl cyclobutabenzoates, cyclobutabenzamides, and alkoxy cyclobutabenzenes.

Examples of some preferred aromatic hydrocarbons with fused cyclobutene rings include methylcyclobutabenzene, ethylcyclobutabenzene, propylcyclobutabenzene, butylcyclobutabenzene, pentylcyclobutabenzene, hexylcyclobutabenzene, benzylcyclobutabenzene, phenylcyclobutabenzene, methyl cyclobutabenzoate, ethyl cyclobutabenzoate, propyl cyclobutabenzoate, butyl cyclobutabenzoate, pentyl cyclobutabenzoate, hexyl cyclobutabenzoate, benzyl cyclobutabenzoate, phenyl cyclobutabenzoate, methoxycyclobutabenzene, ethoxycyclobutabenzene, propoxycyclobutabenzene, butoxycyclobutabenzene, pentoxycyclobutabenzene, hexoxycyclobutabenzene, benzoxycyclobutabenzene, phenoxycyclobutabenzene, N-methylcyclobutabenzamide, N-ethylcyclobutabenzamide, N-propylcyclobutabenzamide, N-butylcyclobutabenzamide, N-pentylcyclobutabenzamide, N-hexylcyclobutabenzamide, N-benzylcyclobutabenzamide, and N-phenylcyclobutabenzamide.

Examples of even more preferred aromatic hydrocarbons with cyclobenzene rings fused thereto are methyl cyclobutabenzoate, ethyl cyclobutabenzoate, propyl cyclobutabenzoate, pentyl cyclobutabenzoate, and hexyl cyclobutabenzoate.

In one of the most preferred embodiments the aromatic hydrocarbon with a cyclobutene ring fused thereto is methyl cyclobutabenzoate.

Hydrocarbyl means herein an organic moiety containing carbon and hydrogen atoms. The term hydrocarbyl includes the following organic moieties: alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aliphatic and cycloaliphatic aralkyl and alkaryl. Aliphatic refers herein to straight- and branched-, and saturated and unsaturated, hydrocarbon chains, that is, alkyl, alkenyl or alkynyl. Cycloaliphatic refers herein to saturated and unsaturated cyclic hydrocarbons, that is cycloalkenyl and cycloalkyl. The term aryl refers herein to biaryl, biphenylyl, phenyl, naphthyl, phenanthranyl, anthranyl and two aryl groups bridged by an alkylene group. Alkaryl refers herein to an alkyl-, alkenyl- or alkynyl-substituted aryl substituent wherein aryl is as defined hereinbefore. Aralkyl means herein an alkyl, alkenyl or alkynyl group substituted with an aryl group, wherein aryl is as defined hereinbefore. $C_{1-20}$ alkyl includes straight- and branched-chain methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl groups.

Cycloalkyl refers to alkyl groups containing one, two, three or more cyclic rings. Cycloalkenyl refers to mono-, di- and polycyclic groups containing one or more double bonds. Cycloalkenyl also refers to cycloalkenyl groups wherein two or more double bonds are present.

Hydrocarbylcarbonyloxy refers to a substituent in which a hydrocarbyl moiety is bonded to a carbonyl moiety which is further bonded to an oxygen atom and includes substituents which correspond to the formula

$$R^2\overset{O}{\overset{\|}{C}}O- .$$

Hydrocarbylcarbonyl refers herein to a substituent which is a hydrocarbyl moiety bonded to a carbonyl moiety and includes substituents which correspond to the formula

$$R^2\overset{O}{\overset{\|}{C}}- \quad .$$

Hydrocarbyloxycarbonyl refers herein to a substituent in which a hydrocarbyl moiety is bonded to an oxygen atom which is further bonded to a carbonyl moiety and includes substituents which correspond to the formula

$$R^2O\overset{O}{\overset{\|}{C}}- \quad .$$

The term carboxamide refers to a substituent which corresponds to the formula

$$-\overset{O}{\overset{\|}{C}}N(R^2)_2$$

wherein $R^2$ is a hydrocarbyl moiety.

The term carbonylhalo refers to a substituent which corresponds to the formula

$$-\overset{\underset{\|}{O}}{C}X$$

wherein X is a halogen.

The term carboxy refers herein to a substituent which corresponds to the formula

$$-\overset{\underset{\|}{O}}{C}OH \quad .$$

The term hydrocarbyloxy refers herein to a substituent which corresponds to the formula

$$R^2\text{-O-}$$

wherein $R^2$ is a hydrocarbyl moiety.

In the process of this invention the ortho alkyl halomethyl aromatic hydrocarbon is dissolved in an inert solvent, and thereafter pyrolyzed to form a cyclobutene ring. Dissolving the aromatic hydrocarbon in a suitable solvent is critical to the invention, as this allows the preparation of the aromatic hydrocarbon with the cyclobutene ring fused thereto in high yields.

In general suitable solvents are those which dissolve the ortho alkyl halomethyl aromatic hydrocarbons and which are stable at pyrolysis conditions. Preferable solvents include benzene, substituted benzenes, biphenyl or substituted biphenyls. Preferred solvents are benzene, toluene, xylene, chlorobenzenes, nitrobenzenes, alkylbenzoates, phenylacetates, or diphenylacetates. The most preferred solvent is xylene.

In general the ratio of solvent to the starting material, the ortho-alkyl halomethyl aromatic hydrocarbon, is such that the starting material is dissolved and results in an acceptable yield of products. It is preferable that the ratio of solvents to starting material be at least 2:1. Preferable solvent to starting material ratios are between 2:1 and 10:1; and more preferred, between 3:1 and 4:1.

During the pyrolysis the starting material dissolved in solvent is exposed to temperatures at which the ortho-alkyl halomethyl aromatic hydrocarbon eliminates a hydrogen halide and forms a cyclobutene ring. Suitable temperatures are those at which this takes place. Preferable temperatures are 550°C or greater. More preferred temperatures are between 550°C and 750°C, with between 700°C and 750°C being most preferred.

The pyrolysis can take place at any pressure at which good yields of the aromatic hydrocarbons with cyclobutene rings fused thereto are prepared. Preferable pressures are between 760 mm and 10 mm of mercury (101.3 and 1.3 kPa). More preferred pressures are between 25 mm and 75 mm of mercury (3.3 and 10.0 kPa), with between 25 mm and 35 mm of mercury (13.3 and 4.7 kPa) being most preferred.

In one preferred embodiment the pyrolysis takes place by flowing a solution of the ortho alkyl halomethyl aromatic hydrocarbon through a hot tube reactor at the pyrolysis temperatures. In this embodiment is preferred to pack the hot tube with a packing material. Any packing material which is inert to the reactants and stable to the reaction conditions is suitable, examples include quartz chips and stainless steel helices.

The product can be recovered by distillation of the materials after pyrolysis. In the embodiment wherein a low boiling solvent is used, the solvent comes off in the first cut of a distillation while the product comes off in the second cut. The starting material is usually left as a residual material in the distillation pot and can thereafter be recycled. When high boiling solvents such as biphenyl, substituted biphenyls or diphenylacetates are used, the product is distilled out and the starting material left in the solvent is recycled.

This process generally results in the preparation of cyclobutene fused aromatic hydrocarbons with a yield of about 40 percent, in more preferred embodiments the yield is about 50 percent.

The following examples are included for illustrative purposes only, and do not limit the scope of the claims or the invention.

Example 1 - Pyrolysis of methyl 3-(chloromethyl)-4-methylbenzoate

The experimental setup is a quartz tube packed with quartz chips. The central portion of the tube is placed in a furnace. A 250 millimeter portion of the tube above the furnace serves as a preheating zone and the temperature in the middle of such preheating zone is between 250°C and 300°C. Attached to the top of the tube is an addition funnel. Attached to the bottom portion of the tube are cold traps and a means for pulling a vacuum on the tube. Methyl 3-(chloromethyl)-4-methylbenzoate (50 g) is dissolved in 200 g of ortho xylene and placed in the addition funnel. The furnace is heated up to 730°C. A vacuum pump is turned on and pressure is adjusted to 25 mm of mercury (3.3 kPa). The solution of methyl 3-(chloromethyl)-4-methylbenzoate is added drop-wise for a period of 1 hour and 15 minutes. Product and unreacted starting material are collected in cold traps. The pyrolytic tube is flushed with 200 ml of acetone after a cooling down period. The acetone solution is combined with the ortho-xylene solution collected in the cold traps. Acetone and ortho-xylene are distilled off with a 16-inch Vigreaux column under normal pressure. When most of the ortho-xylene is distilled, the system is brought to 0.5 mm mercury (67 Pa) and 15.5 g of pure methyl 3,4-cyclobutabenzoate is collected at 61°C. The residue left in the distillation pot is methyl 3-(chloromethyl)-4-methylbenzoate, 23 g.

Experimental Procedure Examples 2-12

A quartz tube packed with quartz chips is placed in an electric furnace such that a 120 mm portion above the furnace serves as a preheating zone, the temperature of which is 250°C. At the top of the quartz tube is inserted an addition funnel. The quartz tube is connected at the bottom to cold traps and a vacuum pump or water aspirator.

A furnace is heated to the desired temperature as indicated by the thermal couple inside a thermal well extended to the middle of the heated zone. Vacuum is then applied. The solution in the addition funnel is then added. The products and unreacted starting material are collected by the cold traps. Product yields are determined by gas chromatography. The material in the addition funnel is the starting material dissolved in ortho-xylene or toluene.

Examples 2-5

In Examples 2-5 the ratio of solvent to starting material is varied. The results are contained in Table I. Table I shows that the pyrolysis of methyl 3-(chloromethyl)--4-methylbenzoate using a solvent to starting material ratio of between 21 and 4 results in good selectivity and yield. The selectivity and material balance goes down when the ratio of solvent to starting material is only 2.

TABLE I

| Experiment | Temp (°C) | Diluent[1] / Substrate | Addition[2] Rate ml/min. | Conversion[3] | Selectivity[4] | Yield[5] | Material Balance[6] |
|---|---|---|---|---|---|---|---|
| 2 | 730 | 21.0 | 2.5 | 57 | 79 | 45 | 89 |
| 3 | 725 | 5.5 | 3.0 | 46 | 70 | 32 | 86 |
| 4 | 725 | 4.0 | 3.0 | 45 | 69 | 31 | 88 |
| 5 | 730 | 2.0 | 2.5 | 66 | 55 | 37 | 71 |

[1]Ratio of diluent (solvent) to substrate.

[2]Addition rate of diluent and substrate to the pyrolysis tube.

[3]Conversion refers to the mole percent of reactants converted to products and by-products.

[4]Selectivity refers to the mole percent of the desired product recovered compared to the total products and by-products.

[5]Yield refers herein to mole percent of the desired product compared to the total reactants fed.

[6]Material balance is the mole percent of the unreacted reactant and desired product compared to the total reactants fed to the reactor.

Examples 6-8

The pressures were varied for the pyrolysis of methyl 3-(chloromethyl)-4-methylbenzoate. The results are contained in Table II. Table II demonstrates that lower reaction pressures result in better yields of product.

TABLE II

| Experiment | Pressure mmHg (kPa) | Temp (°C) | Diluent[1] / Substrate | Addition[2] Rate ml/min. | Conversion[3] | Selectivity[4] | Yield[5] | Material Balance[6] |
|---|---|---|---|---|---|---|---|---|
| 6 | 25 (3.3) | 730 | 21 | 2.5 | 57 | 79 | 45.0 | 89.0 |
| 7 | 150 (20.0) | 700 | 24 | 2.5 | 51 | 46 | 23.5 | 72.0 |
| 8 | 150 (20.0) | 715 | 90 | 2.5 | 70 | 40 | 28.0 | 58.5 |

[1]Ratio of diluent (solvent) to substrate.

[2]Addition rate of diluent and substrate to the pyrolysis tube.

[3]Conversion refers to the mole percent of reactants converted to products and by-products.

[4]Selectivity refers to the mole percent of the desired product recovered compared to the total products and by-products.

[5]Yield refers herein to mole percent of the desired product compared to the total reactants fed.

[6]Material balance is the mole percent of the unreacted reactant and desired product compared to the total reactants fed to the reactor.

Examples 9-12 - Pyrolysis of 2-chloromethyl-1-methylbenzene and methyl 3-(halomethyl)-4--methylbenzoate

In Examples 9-12, 2-chloromethyl-1-methylbenzene and methyl 3-(chloromethyl)-4-methylbenzoate are pyrolyzed. The results are contained in Table III.

TABLE III

| Experiment | Reactant | Temp °C | Pressure mmHg (kPa) | Conversion[1] | Selectivity[2] | Yield[3] | Material Balance[4] |
|---|---|---|---|---|---|---|---|
| 9 | Cl | 710 | 25-35 (3.3-4.7) | 57 | 65 | 37.0 | 80 |
| 10 | Cl $CO_2CH_3$ | 710 | 25-35 (3.3-4.7) | 42 | 63 | 26.5 | 85 |
| 11 | Cl | 700 | 150-175 (20.0-23.3) | 89 | 34 | 30.0 | 41 |
| 12 | Cl $CO_2CH_3$ | 700 | 150-175 (20.0-23.3) | 51 | 46 | 23.5 | 72 |

[1]Conversion refers to the mole percent of reactants converted to products and by-products.

[2]Selectivity refers to the mole percent of the desired product recovered compared to the total products and by-products.

[3]Yield refers herein to mole percent of the desired product compared to the total reactants fed.

[4]Material balance is the mole percent of the unreacted reactant and desired product compared to the total reactants fed to the reactor.

WHAT IS CLAIMED IS:

1. A process for the preparation of an aromatic hydrocarbon with a cyclobutene ring fused to the aromatic hydrocarbon which comprises, dissolving an ortho-alkyl halomethyl aromatic hydrocarbon in an inert solvent and pyrolyzing the solution of ortho-alkyl halomethyl aromatic hydrocarbon in the inert solvent under conditions such that the ortho-alkyl and the halomethyl substituents form a cyclobutene ring thereby forming an aromatic hydrocarbon having a fused cyclobutene ring. The ortho-alkyl group having the structured formula $(R')_2$-CH-, wherein R' is separately in each occurance hydrogen or a $C_{1-20}$ alkyl.

2. The process of Claim 1 wherein the weight ratio of solvent to the ortho alkyl halomethyl aromatic hydrocarbon is at least 2:1.

3. The process of Claim 1 wherein the solvent is benzene, a substituted benzene, diphenyl or a substituted diphenyl.

4. The process of Claim 3 wherein the solvent is a benzene, toluene, xylene, a chlorobenzene, nitrobenzene, alkyl benzoate, phenylacetate, or diphenylacetate.

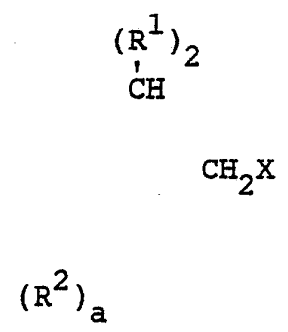
5. The process of Claim 1 wherein the pyrolysis is conducted at a temperature of 550°C or greater.

6. The process of Claim 5 wherein the pyrolysis is conducted at a pressure between 10 and 760 mm Hg (1.3 and 101.3 kPa).

7. The process of Claim 7 wherein the pressure is between 25 and 75 mm Hg (3.3 and 10.0 kPa).

8. The process of Claim 8 wherein the aromatic radical of the substituted aromatic hydrocarbon is benzene, naphthalene, phenanthracene, anthracene, biphenyl, binaphthyl or a diarylalkane.

9. The process of Claim 1 wherein the ortho--alkyl halomethyl aromatic hydrocarbon corresponds to the formula




and the aromatic hydrocarbon with a fused cyclobutene ring corresponds to the formula

$(R^1)_2$

$(R^2)_a$

wherein

$R^1$ is separately in each occurrence hydrogen or $C_{1-20}$ alkyl; and

$R^2$ is separately in each occurrence carbonyloxyhydrocarbyl, oxycarbonylhydrocarbyl, carboxamide, carboxy, carbonylhalo, cyano, nitro, hydroxy, hydrocarbyloxy or halo;

X is chloro or bromo; and

a is an integer of between 0 and 4, inclusive.

10. The process of Claim 9 wherein $R^1$ is hydrogen or $C_{1-3}$ alkyl; $R^2$ is carbonyloxyhydrocarbyl, oxycarbonylhydrocarbyl, carboxamide, carboxy, carbonylhalo, nitro or hydrocarbyloxy; X is chlorine; and a is 1.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US85/00939

**I. CLASSIFICATION OF SUBJECT MATTER** (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC 3

C07C 39/17, 51/09

**II. FIELDS SEARCHED**

Minimum Documentation Searched [4]

| Classification System | Classification Symbols |
|---|---|
| U.S. | 260/1,8,80,108,138,410.9R, 465R.H, 544F,L,P; 560/405,488;562/153,155,172;570/129,143,182,183; |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

**III. DOCUMENTS CONSIDERED TO BE RELEVANT** [14]

| Category * | Citation of Document, [16] with indication, where appropriate, of the relevant passages [17] | Relevant to Claim No. [18] |
|---|---|---|
| Y | N Journal of the American Chemical Society, Vol. 91 No. 27 December 1969 A.G. Louden et al. "Gas-Phase Eliminations. XI. The pyrolysis of -Chloro-o-xylene" | 1-16 |
| Y | N Tetrahedron Letters, No. 46 1978 Peter Schiess et al "Preparation of Benzocyclobutenes by Flash Vacuum Pyrolysis" | 1-16 |
| Y | N Tetrahedron Letters, No. 44 1978 V. Boekelheide et al, "The Use of Benzocyclobutenes as Intermediates in Synthesis of Multibridged Cyclophanes". | 1-16 |
| Y | N Pyrolytic Methods in Organic Chemistry, Brown, Academic Press, New York, (1980) pages 105-6 | 1-16 |

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**IV. CERTIFICATION**

| Date of the Actual Completion of the International Search [2] | Date of Mailing of this International Search Report [2] |
|---|---|
| 17 July 1985 | 01 AUG 1985 |
| **International Searching Authority [1]** | **Signature of Authorized Officer [10]** |
| ISA/US | J. T. Sullivan JTS |

**FURTHER INFORMATION CONTINUED FROM THE FIRST SHEET**
(Not for publication)

The formulas in the specification are incomplete; see page 3, line 21 and page, 6, line 13.

The formulas in claim 9 are incomplete. Applicants have to drawn in the rings.