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AMENDED

AUSTRALIA 16 MAR 1988 PATENT OFFICE

(a) convention

AUSTRALIA

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(b) Delete one

APPLICATION FOR A (b) STANDARD/PETTY PATENT

(c) Insert FULL name(s) of applicant(s)

I/We (c) THE DOW CHEMICAL COMPANY

608858

(d) Insert FULL address(es) of applicant(s)

of (d) 2030 Dow Center, Abbott Road,
Midland, Michigan 48640,
United States of America

(e) Delete one

hereby apply for the grant of a (e) Standard/Petty Patent for an invention entitled

(f) Insert TITLE of invention

(f) PROCESS FOR PREPARING MONOHALOGENATED CYCLOBUTARENES

(g) Insert "complete" or "provisional" or "petty patent"

which is described in the accompanying (g) complete specification.

(Note: The following applies only to Convention applications)

Details of basic application(s)

(h) Insert number, country and filing date for the/or each basic application

	Application No.	Country	Filing Date
(h)	064,714	United States of America	22 June, 1987

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 15-1-91

Address for Service: PHILLIPS ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia 3000

(i) Insert date of signing

Dated (i) 15 June, 1988

(j) Signature of applicant(s) (For body corporate see headnote*)

(k) Corporate seal if any

(k)

(j) PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
THE DOW CHEMICAL COMPANY

Note: No legalization or other witness required

PHILLIPS ORMONDE AND FITZPATRICK
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P17/2/83

AUSTRALIA

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Patent Declaration

DECLARATION FOR A PATENT APPLICATION

INSTRUCTIONS
(a) Insert "Convention" if applicable
(b) Insert FULL name(s) of applicant(s)
(c) Insert "of addition" if applicable
(d) Insert TITLE of invention

In support of the (a) Convention application made by (b)
THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road,
Midland, Michigan 48640, U.S.A.

(hereinafter called "applicant(s)") for a patent (c) for an invention entitled (d)
PROCESS FOR PREPARING MONOMBROAMINED CYCLOBUTARENES

(e) Insert FULL name(s) AND address(es) of declarant(s) (See headnote *)

I/[redacted] (e) Richard G. Waterman, General Patent Counsel
THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road,
Midland, Michigan 48640, U.S.A.
do solemnly and sincerely declare as follows:

1. ~~I am/We are the applicant(s).~~
(or, in the case of an application by a body corporate)
1. I am/~~We are~~ authorized to make this declaration on behalf of the applicant(s).
2. ~~I am/We are the actual inventor(s) of the invention.~~
(or, where the applicant(s) is/are not the actual inventor(s))
2. (f) Ming-Biann Liu, 386 Mt. Sequoia Place, Clayton, State of California 94517 United States of America

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

(g) Recite how applicant(s) derive(s) title from actual inventor(s) (See headnote **)

is/~~are~~ the actual inventor(s) of the invention and the facts upon which the applicant(s) is/~~are~~ entitled to make the application are as follows:
(g) The applicant Company is the assignee of the said invention from the said actual inventor(s).

(Note: *Paragraphs 3 and 4 apply only to Convention applications)*

(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

3. The basic application(s) for patent or similar protection on which the application is based is/~~are~~ identified by country, filing date, and basic applicant(s) as follows:
(h) United States of America
June 22, 1987
Ming-Biann Liu

4. The basic application(s) referred to in paragraph 3 hereof was/~~were~~ the first application(s) made in a Convention country in respect of the invention the subject of the application.

(k) Insert PLACE of signing
(l) Insert DATE of signing
(m) Signature(s) of declarant(s)
Note: No legalization or other witness required

Declared at (k) Midland, Michigan, 48640, U.S.A.
Dated (l) June 9 1988

THE DOW CHEMICAL COMPANY

CORP. SEAL

To: The Commissioner of Patents By: [signature]
RICHARD G. WATERMAN
General Patent Counsel

Agent:

No legalization or other witness required

(12) PATENT ABRIDGMENT (11) Document No. AU-B-18206/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 608858

(54) Title
PROCESS FOR PREPARING MONOHALOGENATED CYCLOBUTARENES

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(56) Prior Art Documents
US 4540763

(57) Claim

1. A method of preparing monohalogenated cyclobutarenes consisting essentially of halogenating a cyclobutarene in the presence of an organic complexing agent, an acid scavenger, or water provided that the halogenating agent is not N-bromosuccinimide or pyridinium perbromide hydrobromide.

5. A method as claimed in any one of claims 1 to 4 wherein the organic complexing agent is selected from the group consisting of saturated aliphatic alcohols and diols having less than 10 carbon atoms; aliphatic polymeric diols having an average molecular weight ranging from 100 to 15,000; saturated aliphatic ethers having less than 10 carbon atoms; saturated cyclic ethers; saturated quaternary ammonium salts; saturated aliphatic carboxylic acids and their anhydrides having less than 10 carbon atoms; dimethyl formamide; dimethyl sulfoxide; and mixtures of these complexing agents.

.../2

8. A method as claimed in any one of claims 1 to 7 wherein the acid scavenger is an organic acid scavenger selected from the group consisting of epoxides having less than 10 carbon atoms; aliphatic tertiary alcohols having less than 10 carbon atoms; alkali metal and alkali earth metal salts of aliphatic alcohols having less than 10 carbon atoms; aliphatic primary, secondary, and tertiary amines; heterocyclic compounds selected from the group consisting of pyridine and picoline; and triarylphosphines; or an inorganic acid scavenger selected from the group consisting of alkali metal and alkali earth metal bases, and carbonates and bicarbonates of alkali metal and alkali earth metals.

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COMPLETE SPECIFICATION
(ORIGINAL)

Class Int. Class

Application Number:
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Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

APPLICANT'S REFERENCE: 34,759-F

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Complete Specification for the invention entitled:

PROCESS FOR PREPARING MONOBROMINATED CYCLOBUTARENES
Process for Preparing Monobutogenated Cyclobutarenes

Our Ref : 97068
POF Code: 1037/1037

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

PROCESS FOR PREPARING MONOHALOGENATED CYCLOBUTARENES

This invention relates to a process for preparing halogenated organic compounds. More specifically, it relates to a process for preparing monohalogenated cyclobutarenes.

Monohalogenated cyclobutarenes are intermediates for the preparation of high performance monomeric and polymeric compositions for the electronics and aerospace industries. U.S. Patent 4,540,763 discloses that monohalogenated cyclobutarenes can be processed to prepare poly(cyclobutarene) polymeric compositions. These compositions possess thermal stability at high temperatures, as well as chemical resistance and low sensibility to water.

Processes for preparing monohalogenated cyclobutarenes are difficult because multiple halogenation reactions occur and the strained cyclobutane ring of the cyclobutarene is easily susceptible to ring-opening side reactions (see J. B. F. Lloyd et al., Tetrahedron, 20, pp. 2185-94 (1964)). U.S. Patent 4,540,763 discloses a process for

preparing monobrominated cyclobutarenes which involves diluting a cyclobutarene in acetic acid and then contacting the solution with pyridinium perbromide hydrobromide in the presence of a mercuric acetate catalyst. The reaction occurs over a four day period and uses approximately 300 percent excess brominating agent. J. B. F. Lloyd et al., Tetrahedron, 21, pp. 245-54, (1965), disclose a process for preparing monobrominated benzocyclobutene which involves diluting benzocyclobutene in a 95 percent aqueous solution of acetic acid and then contacting the solution with molecular bromine in the presence of an iodine catalyst. The yield of monobrominated benzocyclobutene is 78 percent after 48 hours. Unfortunately, both of these processes require large quantities of brominating agent to complete a very slow bromination reaction. Also, both processes require either a heavy metal catalyst or a halogen catalyst. The residual catalyst that inevitably finds its way into the final product is detrimental for electronics and aerospace industry applications. Furthermore, these catalysts create environmental problems related to their disposal.

Therefore, it would be desirable to have a process for preparing monohalogenated cyclobutarenes that does not require a halogen catalyst or a heavy metal catalyst. It would also be desirable to have a process providing a faster halogenation reaction highly selective to monohalogenated cyclobutarenes without requiring excessive quantities of halogenating agent.

This invention is a method of preparing monohalogenated cyclobutarenes consisting essentially of halogenating a cyclobutarene in the presence of an organic complexing agent, an acid scavenger, or water.

Surprisingly, reaction rates faster than the rates disclosed in the prior art are achieved by the method of this invention without requiring a catalyst. In addition, the reaction is highly selective to monohalogenated cyclobutarenes and neither requires excessive quantities of halogenating agent nor creates an environmental problem related to the disposal of the catalysts.

The monohalogenated cyclobutarenes of this invention are useful as intermediates for the preparation of high performance monomeric and polymeric compositions for the electronics industry.

When used herein and in the claims the term "cyclobutarene" refers to a compound containing at least one aromatic ring to which is fused one or more cyclobutane rings or one or more substituted cyclobutane rings. An aromatic ring contains $(4N + 2)\pi$ electrons as described in Morrison and Boyd, Organic Chemistry, 3rd Edition, (1973). Suitable compounds containing at least one aromatic ring include benzene, naphthalene, biphenyl, binaphthyl, phenanthrene, anthracene, and diphenylbenzene. The aromatic ring of the cyclobutarene can be substituted with groups stable to the bromination reaction, including but not limited to groups such as methyl, methoxy, and acetate. Heterocyclic compounds such as pyridine and picoline are also included. Preferred compounds are benzene, naphthalene, and biphenyl. The most preferred compound containing at least one aromatic ring is benzene. Therefore, the most preferred cyclobutarene is benzocyclobutene.

As disclosed in U.S. Patent 4,570,011, cyclobutarenes useful in this invention can be prepared by dissolving an ortho alkyl halomethyl aromatic hydrocarbon, such as ortho methylchloromethylbenzene, in an inert solvent, and then pyrolyzing the solution under suitable reaction conditions.

"Halogenating" refers to the introduction of halogen into an organic compound by treating the compound with a halogenating agent. Suitable halogenating agents useful in this invention are those compounds which are capable of reacting with the aromatic ring of the cyclobutarene to break the carbon-hydrogen bond and to form a carbon-halogen bond under the reaction conditions. Halogenating agents useful for halogenating cyclobutarenes are disclosed in H. P. Braendlin et al. Friedel-Crafts and Related Reactions, Vol. III, Chapter 46, pp. 1517-1593, John Wiley & Sons, New York (1964); Wagner et al. Synthetic Organic Chemistry, pp. 98-147, John Wiley & Sons, New York, (1965); and March, Advanced Organic Chemistry, 34d ed. pp. 476-479, John Wiley & Sons, New York (1985). Preferred halogenating agents are brominating and chlorinating agents. The most preferred halogenating agent is a brominating agent.

The brominating agents that can be employed in this invention can include molecular bromine, bromine chloride, pyridinium perbromide hydrobromide, dioxane dibromide, and N-bromosuccinimide. Preferred brominating agents include molecular bromine and bromine chloride. The most preferred brominating agent is molecular bromine.

Preferred chlorinating agents include molecule chlorine N-chlorosuccinimide, and t-butyl hypochlorite. Preferred iodinating agents include molecular iodine and iodine monochloride.

The monohalogenated cyclobutarenes useful in this invention are prepared by halogenating a cyclobutarene. The term "monohalogenated" refers to the replacement of one hydrogen atom on the aromatic ring with one halogen atom. The products produced from the halogenation of the cyclobutarene include not only the monohalogenated cyclobutarenes but also small quantities of hydrogen halide, unreacted halogenating agent and undesirable side reaction products. The hydrogen halide can either dissolve in the reaction mixture or evolve from the reaction mixture as a gas.

The organic complexing agents that improve the selectivity of the reaction to monohalogenated cyclobutarenes are organic compounds that will donate electrons to form donor-acceptor adducts with the unreacted halogenating agent and the hydrogen halide ~~produced during the reaction. The adduct formed~~ reduces the reactivity of the halogenating agent and hydrogen halide with the cyclobutane ring of the cyclobutarene and therefore reduces formation of undesirable side products. A. J. Downs et al., Comprehensive Inorganic Chemistry, Chapter 26, pp. 1196-1197 and pp. 1201-1209, New York, New York, (1973), discuss the crystalline structure of halogen adducts based on X-ray diffraction studies. They describe organic compounds which form halogen adducts and the factors influencing their stability. They also describe the relative capacities of organic compounds ~~to donate electrons. Preferably, the organic complexing~~

produced during the reaction. Accordingly, when used herein and in the claims "organic complexing agent" refers to an organic compound that will donate electrons to form donor-acceptor adducts with the unreacted halogenating agent and the hydrogen halide produced during the reaction. The adduct formed reduces the reactivity of the halogenating agent and hydrogen halide with the cyclobutane ring of the cyclobutarene and therefore reduces formation of undesirable side products. A.J. Downs et al., Comprehensive Inorganic Chemistry, Chapter 26, pp. 1196-1197 and pp 1201-1209, New York, New York, (1973), discuss the crystalline structure of halogen adducts based on X-ray diffraction studies. They describe organic compounds which form halogen adducts and the factors influencing their stability. They also describe the relative capacities of organic compounds to donate electrons. Preferably, the organic complexing

agent has an electron donor capacity equal to or slightly greater than the electron donor capacity of the cyclobutarene.

Suitable organic complexing agents include aliphatic alcohols and diols having less than 10 carbon atoms, such as methanol, isobutyl alcohol, and ethylene glycol; aliphatic polymeric diols having an average molecular weight ranging from 100 to 15,000, such as the commercial grades of polyethylene glycol and polypropylene glycol; saturated aliphatic ethers having less than 10 carbon atoms, such as ethylene glycol ethyl ether and tripropylene glycol methyl ether; saturated cyclic ethers such as dioxane and 12-crown-4 ether; saturated aliphatic carboxylic acids and their anhydrides having less than 10 carbon atoms, such as acetic acid and acetic anhydride; other complexing agents such as dimethyl formamide and dimethyl sulfoxide; and mixtures of these organic complexing agents. Preferred organic complexing agents are methanol and ethylene glycol ethyl ether. The most preferred organic complexing agent is methanol.

Other organic complexing agents that improve the selectivity of the reaction to monohalogenated cyclobutarenes include saturated quaternary ammonium salts, such as tetraalkylammonium salts and trialkylamine salts. Although these compounds do not donate electrons to form donor-acceptor adducts, their effectiveness as complexing agents has been demonstrated.

The Dictionary of Scientific and Technical Terms, McGraw-Hill, Second Edition (1978) defines a scavenger as "a substance added to a mixture or other

system to remove or inactivate impurities". Acid scavengers useful in this invention remove or inactivate hydrogen halide produced during the halogenation by reacting with the hydrogen halide to form a side product. The scavenger does not react with the cyclobutarene. Preferably, the scavenger reacts readily with hydrogen halide but does not react readily with the halogenating agent to prevent the halogenation of the cyclobutarene. The acid scavenger can be organic or inorganic.

Suitable organic acid scavengers include epoxides having less than 10 carbon atoms, such as ethylene oxide, propylene oxide, epichlorohydrin, and epibromohydrin; aliphatic tertiary alcohols having less than 10 carbon atoms, such as tertiary butyl alcohol; aliphatic primary, secondary and tertiary amines, such as ethylamine, diethylamine, and triethylamine; heterocyclic compounds such as pyridine and picoline, and triarylphosphines such as triphenylphosphine. The preferred scavengers are the epoxides having less than 10 carbon atoms and the tertiary amines. The most preferred epoxide is epichlorohydrin and the most preferred tertiary amine is triethylamine.

Suitable inorganic acid scavengers include alkali metal and alkali earth metal salts of alcohols and carboxylic acids, such as sodium methylate, sodium ethylate, and sodium acetate; alkali metal and alkali earth metal bases, such as sodium hydroxide and calcium hydroxide; and carbonates and bicarbonates of alkali metal and alkali earth metals, such as sodium bicarbonate and potassium carbonate.

When the cyclobutarene is halogenated in the presence of water, the water acts in a manner similar to that of the organic complexing agent by forming donor-acceptor adducts with the unreacted halogenating agent and the hydrogen halide.

In a preferred embodiment of this invention, the solubility of hydrogen halide produced during halogenation in the reaction mixture is reduced. The reduced solubility will increase the quantity of hydrogen halide that will evolve from the reaction mixture as a gas. Since more hydrogen halide will evolve from the reaction mixture as a gas, there will be less hydrogen halide in the reaction mixture that can react with the cyclobutane ring of the cyclobutarene to produce undesirable side products. Therefore, an increased selectivity of monohalogenated cyclobutarene will result.

One method of reducing the solubilit of hydrogen halide in the reaction mixture is to dilute the cyclobutarene in an appropriate nonreacting diluent before halogenation. Appropriate diluents are those in which the solubility of hydrogen halide is low. Ahmed et al., Journal of Applied Chemistry, 20 , pp. 109-116, (April 1970), disclose the solubilities of hydrogen halides in various diluents. Suitable diluents that can be employed in this invention include methylene chloride, chloroform, carbon tetrachloride, ethylene dichloride, bromochloromethane, and hexane. The preferred diluents are methylene chloride, chloroform, and bromochloromethane. The most preferred diluent is methylene chloride.

Certain organic complexing agents can also act as appropriate nonreacting diluents. Examples of such organic complexing agents include acetic acid, methanol, and water.

The mole ratio of the cyclobutarene to the complexing agent or water employed in the practice of this invention can range from 0.001:1 to 100:1. A more preferable range is from 0.005:1 to 70:1. The most preferable range is from 0.05:1 to 6.0:1. The mole ratio of the cyclobutarene to the scavenger employed in the practice of this invention can range from 0.1:1 to 100:1. A more preferable range is from 0.3:1 to 20:1. The most preferable range is from 0.5:1 to 2.0:1.

If a diluent is employed to dilute the cyclobutarene before halogenation, the weight ratio of the diluent to the cyclobutarene can range from 0.1:1 to 100:1. A more preferable range is from 0.5:1 to 20:1. The mole ratio of the brominating agent to the cyclobutarene can range from 0.1:1 to 2.0:1. A more preferable range is from 0.90:1 to 1.10:1.

The operating temperature and pressure of the reaction system are limited solely by practical considerations. The temperature can range from the freezing point to the boiling point of the reaction mixture. Preferably, the operating temperature ranges from 25°C to 60°C. Although the halogenation reaction will proceed at both high and low operating pressures, it is preferable to run as close to atmospheric pressure as possible because higher pressures will increase the solubility of the hydrogen halide in the reaction system and therefore generate more side

reactions. Also, high operating pressures necessitate the use of more expensive pressure rated equipment.

In a preferred embodiment of this invention, the halogenating agent is added continuously or periodically to the reaction mixture to control the evolution of gaseous hydrogen halide. By controlling the evolution of the gaseous hydrogen halide, the operating pressure of the system can be maintained as close to atmospheric pressure as possible.

The halogenation reaction proceeds almost instantaneously when the halogenating agent contacts the cyclobutarene. In most instances, the required reaction time depends on the rate of addition of the halogenating agent to the reaction system. The rate of addition of the halogenating agent depends on the ability of the system to remove the gaseous hydrogen halide and the design pressure of the reactor.

The selectivity of the reaction to monohalogenated cyclobutarenes decreases with conversion because the monohalogenated cyclobutarenes prepared from the halogenation can react further with the reaction mixture to form undesirable side products. Advantageously, the monohalogenated cyclobutarenes are separated quickly from the reaction mixture. In preferred embodiments of this invention, the selectivity will range from 75 mole percent to 95 mole percent. Selectivity is defined as the mole percentage of the reacted cyclobutarene that forms monohalogenated cyclobutarenes.

After the halogenation reaction, the monohalogenated cyclobutarenes can easily be separated

from the side products produced by the reaction. One method of separation is to fractionally distill all of the impurities from the reaction system. Another method of separation involves adding an aqueous solution of a reducing agent, such as sodium metabisulfite, to neutralize the residual halogenating agent and to extract the hydrogen halide from the organic phase of the reaction mixture to the aqueous phase. The aqueous phase can then be physically separated from the organic phase and then the organic phase can be fractionally distilled to recover the monohalogenated cyclobutarenes. Preferably, the recovered monohalogenated cyclobutarenes have a purity of at least 97 percent by weight.

The recovered monohalogenated cyclobutarenes are useful intermediates which can be processed to prepare poly(cyclobutarene) monomeric and polymeric compositions. U.S. Patent 4,540,763 discloses methods of preparing these compositions from monohalogenated cyclobutarenes. The polymeric compositions have excellent thermal stability at high temperatures, good chemical resistance to most industrial solvents, and a low sensitivity to water. These properties are highly desirable for applications in the electronics and aerospace industries.

The following examples are illustrative of this invention. All percentages are mole percent unless otherwise indicated.

Example 1

2005 grams (g) Benzocyclobutene (19.25 moles), 2000 g methylene chloride (23.55 moles) and 200 g

methanol (6.24 moles) were charged to a jacketed, 8 liter cylindrical 3-neck round bottom reactor equipped with a mechanical stirrer, a digital thermocouple, and a reflux condenser connected to a caustic scrubber. The mixture was heated to 40°C by recirculating an aqueous solution of ethylene glycol from a constant temperature bath through the jacket. 3275 g Bromine (20.49 moles) was fed to the reactor at a constant flow rate of 728 g/hr. During the addition, the temperature increased to a range between 48°C and 57.5°C and reflux was observed. A sample of the reaction mixture was taken each hour for 4 hours. Another sample was taken after 4 hours and 30 minutes when all of the bromine has been fed to the reactor. The residual bromine of each sample was neutralized with the requisite amount of an aqueous solution of sodium metabisulfite. Each organic layer was separated and analyzed using a capillary gas chromatograph to determine its composition. A final sample of the reaction mixture was taken after 5 hours and 30 minutes. It was washed with aqueous sodium metabisulfite and the organic layer was separated and analyzed in a similar manner. The analysis of each sample is shown in Table I.

TABLE I

Reaction Time (Hours)	Unreacted Benzo-cyclobutene (Percent)	Mono-brominated Benzo-cyclobutenes (Percent)	2-Bromo-phenethyl Bromide (Percent)	Multi-brominated Benzo-cyclobutene (Percent)	Phenethyl Bromide (Percent)	Selectivity (Percent)
1.0	84.9	13.7	1.5	0	0	91
2.0	58.4	36.9	4.6	0	0	89
3.0	38.1	54.7	6.7	0.2	0.	88
4.0	19.2	70.1	8.9	1.1	0.6	87
4.5*	10.0	77.0	10.2	1.9	0.9	86
5.5	4.4	81.0	10.9	2.7	1.1	85

*Bromine addition complete

Table I indicates that a significantly improved selectivity of the reaction to monobrominated benzocyclobutenes is obtained by the method of this invention without the use of the catalysts of the prior art. Table I also indicates high selectivities are achieved at much faster reaction rates than the rates achieved by the prior art.

Example 2

100.95 g Benzocyclobutene (0.969 moles), 115.52 g methylene chloride (1.36 moles) and 6.00 g methanol (0.187 moles) were charged to the same reactor as that of Example 1 equipped with a 500 ml dropping funnel. The mixture was heated to 40°C. 163.4 g Bromine (1.022 moles) was added dropwise to the reaction mixture through the dropping funnel. During the addition, the temperature increased to 44.2°C and reflux was observed. After 78 minutes the addition of bromine was completed. After 16 hours, the residual bromine of the reaction mixture was neutralized with 200 ml of an aqueous solution containing 10 g of sodium metabisulfite. The organic layer was separated and analyzed using a capillary gas chromatograph. The analysis indicates that the product contains 3.7 percent unreacted benzocyclobutene, 81.2 percent monobrominated benzocyclobutenes, 6.5 percent 2-bromophenethylbromide, 8.4 percent multibrominated benzocyclobutenes and less than 0.3 percent phenethyl bromide.

Example 3

1.6 g Bromine (104 percent theoretical) was added to a solution containing 1 g benzocyclobutene and

0.1 g methanol at room temperature. After 12 hours a sample of the reaction mixture was washed with aqueous sodium metabisulfite. The organic layer was separated and analyzed using a capillary gas chromatograph. The analysis indicates that the product contains 24.8 percent benzocyclobutene, 56.5 percent monobrominated benzocyclobutenes, 9.1 percent 2-bromophenethyl bromide, 9.3 percent multibrominated benzocyclobutenes, and 0.3 percent phenethyl bromide.

Example 4

In each of a series of runs, 1.6 g bromine was added to a solution containing 4 g methylene chloride, 1 g benzocyclobutene and 0.1 g of one of several selected complexing agents (or water) at room temperature. After 12 hours a sample of the reaction mixture was washed with aqueous sodium metabisulfite. The organic layer was separated and analyzed using a capillary gas chromatograph to determine the percent conversion and the percent selectivity. The conversion and selectivity were compared to a first run in which neither the complexing agent (or water) nor methylene chloride were added and a second run in which the complexing agent (or water) was not added. Percent conversion is defined as the mole percentage of benzocyclobutene that reacted. The results are shown in Table II.

TABLE II

Complexing Agent(or Water)	Diluent	Conversion (Percent)	Selectivity (Percent)
None*	None	92.3	71
None*	Methylene chloride	83.1	76
Methanol	Methylene chloride	96.0	86
Water	Methylene chloride	90.3	81
Ethyl Glycol Ethyl Ether	Methylene chloride	87.7	87
Glacial Acetic Acid	Methylene chloride	94.5	81
Tetra(n-butyl) Ammonium Hydrogen Sulfate	Methylene Chloride	92.8	83

*Not an embodiment of this invention.

Table II indicates that a high selectivity of the reaction to monobrominated benzocyclobutenes is obtained by the method of the present invention using various complexing agents or water. The selectivities of the two runs obtained without the complexing agent (or water) are poor relative to the selectivities obtained according to the present invention.

Example 5

1.6 g Bromine was added to a solution containing 1 g benzocyclobutene and 4 g of methanol at room temperature. After 12 hours, a sample of the

reaction mixture was washed with aqueous sodium metabisulfite. The organic layer was separated and analyzed using a capillary gas chromatograph to determine the percent conversion and the percent selectivity. The experiment was repeated replacing the 4 g of methanol with 4 g of water. The results are shown in Table III.

TABLE III

Complexing Agent(or Water)	Diluent	Conversion (Percent)	Selectivity (Percent)
Methanol	None	50.5	85
Water	None	92.0	81

Table III indicates that a high selectivity of the reaction to monobrominated benzocyclobutenes is obtained without the use of a diluent.

Example 6

The procedure of Example 4 was followed, except that the methylene chloride diluent was replaced with various diluents listed in Table IV and the complexing agent employed was methanol. The results are shown in Table IV.

TABLE IV

Complexing Agent	Diluent	Conversion (Percent)	Selectivity (Percent)
Methanol	95 percent Acetic Acid	73.0	82
Methanol	Chloroform	88.2	86
Methanol	Carbon Tetrachloride	82.5	80
Methanol	Ethylene Dichloride	94.9	81
Methanol	Bromochloro-methane	87.7	84
Methanol	Hexane	80.9	81
Methanol	Water	83.0	77

Table IV indicates that a high selectivity of the reaction to monobrominated benzocyclobutenes is still obtained using various diluents other than methylene chloride.

Example 7

The procedure of Example 4 was followed, except that the complexing agents (or water) were replaced with various scavengers listed in Table V. The results are shown in Table V.

Table V

Scavenger	Molar ratio of Scavenger to Benzo-cyclobutene	Diluent	Conversion (Percent)	Selectivity (Percent)
T-Butyl Alcohol	0.14	Methylene chloride	75.6	78
Epichloro-hydrin	1.0	Methylene Chloride	85.1	80
Triethyl-amine	0.10	Methylene Chloride	78.8	85
Sodium Methylate	1.0	Methylene Chloride	44.8	80

Table V indicates that a high selectivity of the reaction to monobrominated benzocyclobutenes is obtained by the method of the present invention using various scavengers instead of complexing agents or water.

The claims defining the invention are as follows:

1. A method of preparing monohalogenated cyclobutarenes consisting essentially of halogenating a cyclobutarene in the presence of an organic complexing agent, an acid scavenger, or water provided that the halogenating agent is not N-bromosuccinimide or pyridinium perbromide hydrobromide.

2. A method as claimed in claim 1 wherein the halogenating agent is a brominating agent or a chlorinating agent.

3. A method as claimed in claim 2 wherein the brominating agent is selected from the group consisting of molecular bromine or bromine chloride.

4. A method as claimed in any one of claims 1 to 3 wherein the cyclobutarene is diluted in a nonreacting diluent selected from the group consisting of methylene chloride, ethylene dichloride, chloroform, carbon tetrachloride, bromochloromethane, hexane, acetic acid, methanol, and water before halogenation.

5. A method as claimed in any one of claims 1 to 4 wherein the organic complexing agent is selected from the group consisting of saturated aliphatic alcohols and diols having less than 10 carbon atoms; aliphatic polymeric diols having an average molecular weight ranging from 100 to 15,000; saturated aliphatic ethers having less than 10 carbon atoms; saturated cyclic ethers; saturated quaternary ammonium salts; saturated aliphatic carboxylic acids and their anhydrides having less than 10 carbon atoms; dimethyl formamide; dimethyl sulfoxide; and mixtures of these complexing agents.

6. A method as claimed in any one of claims 1 to 5 wherein the mole ratio of the cyclobutarene to the organic complexing agent or water ranges from 0.001:1 to 100:1.

7. A method as claimed in any one of claims 2 to 6 wherein the acid scavenger reacts readily with hydrogen bromide but does not react readily with the brominating agent.

8. A method as claimed in any one of claims 1 to 7 wherein the acid scavenger is an organic acid scavenger selected from the group consisting of epoxides having less than 10 carbon atoms; aliphatic tertiary alcohols having less

than 10 carbon atoms; alkali metal and alkali earth metal salts of aliphatic alcohols having less than 10 carbon atoms; aliphatic primary, secondary, and tertiary amines; heterocyclic compounds selected from the group consisting of pyridine and picoline; and triarylphosphines; or an inorganic acid scavenger selected from the group consisting of alkali metal and alkali earth metal bases, and carbonates and bicarbonates of alkali metal and alkali earth metals.

9. A method as claimed in any one of claims 1 to 8 wherein the mole ratio of the cyclobutarene to the acid scavenger ranges from 0.1:1 to 100:1.

10. A method as claimed in any one of claims 1 to 9 wherein the weight ratio of diluent to the cyclobutarene ranges from 0.1:1 to 100:1.

11. A method as claimed in any one of claims 2 to 10 wherein the mole ratio of the brominating agent to the cyclobutarene ranges from 0.1:1 to 2.0:1.

12. A method as claimed in claim 1 substantially as hereinbefore described with reference to any one of the examples.

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