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3,090,817

PARTIAL DEHYDROHALOGENATION OF HALOALKYLHALOBICYCLOALKENIC COMPOUNDS

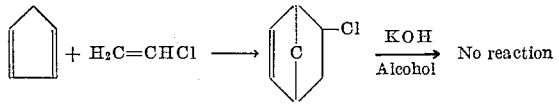
Louis Schmerling, Riverside, Ill., assignor to Universal Oil Products Company, Des Plaines, Ill., a corporation of Delaware

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18 Claims. (Cl. 260—648)

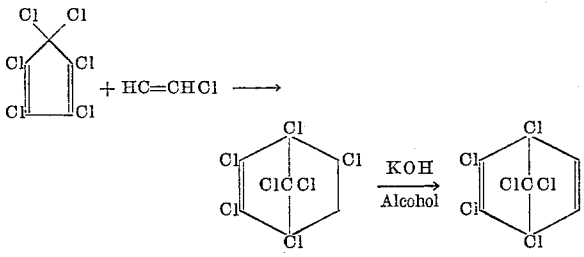
This application is a continuation-in-part of my co-pending application Serial No. 803,587, filed April 2, 1959, now abandoned, which was a continuation-in-part of my co-pending application Serial No. 580,468, filed April 25, 1956, now abandoned.

The present invention relates to methods for partially dehydrohalogenating certain haloalkylhalobicycloolefinic compounds and more particularly to a method of dehydrohalogenating haloalkylhalobicycloheptenes.

Heretofore it has been indicated that bicycloalkadienes could not be prepared by dehalogenating halobicycloalkenes obtained by the condensation of a cycloalkadiene with a haloolefin. For example, attempts have been made, as disclosed in a paper by Roberts et al., Journal of the American Chemical Society, 72, 3329 (1950), and in Belgian Patent No. 498,176, issued to J. Hyman et al., to dehydrochlorinate 5-chlorobicyclo[2.2.1]-2-heptene to form bicyclo[2.2.1]-2,5-heptadiene, also known as 2,5-norbornadiene. This is illustrated by the following equation:



On the other hand, partial dehalogenation of the condensation product of a halogenated cycloalkadiene, namely, hexachlorocyclopentadiene and vinyl chloride may be carried out as shown by the following equations:



However, this dehydrochlorination reaction occurs because of the presence of the six chlorine atoms on one ring of the molecule, said chlorine atoms serving to activate the chlorine atom on the second ring. As hereinbefore stated it has been shown that the reaction product of a conjugated cycloalkadiene such as an unhalogenated cyclopentadiene and a monohaloolefin will not undergo dehydrohalogenation when subjected to the operating conditions of prior processes, the single halogen atom being too inert to undergo reaction with the dehydrohalogenating agent.

However, I have now discovered that the products of the Diels-Alder condensation of cycloalkadienes with a particular class of polyhaloolefins contain active halogens and, contrary to the teaching of the prior art, may be partially dehydrohalogenated to introduce an olefinic bond into a compound having the bicycloheptane ring system which previously was regarded as not susceptible to dehydrohalogenation, thus forming the desired halo-substituted bicycloalkenes. The compounds which I subject to dehydrohalogenation are characterized by the presence of halogen on only one of the rings and

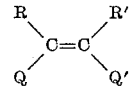
on a side-chain alkyl group. Furthermore, not more than two halogen atoms are attached to the ring. That these compounds undergo dehydrohalogenation is unexpected; the very fact that the literature of the prior art now known shows that a cyclopentadiene-vinyl chloride adduct cannot be dehydrochlorinated while the hexachlorocyclopentadiene-vinyl chloride adduct can be dehydrochlorinated would tend to lead away from the process of the present invention inasmuch as it would appear that a chlorine atom of a bicyclic chlorinated compound cannot be removed by treatment with a dehydrochlorinating agent unless one of the rings is completely chlorinated.

It is therefore an object of this invention to prepare a halo-substituted alkylbicycloalkadiene by partially dehydrohalogenating a haloalkylhalobicycloalkene.

The term "bicycloalkadiene" as used hereinafter in the specification and appended claims, refers to those compounds in which both double bonds are in the ring and to those compounds in which one of the double bonds is in the ring, the other double bond being exo thereto. The expression "halo-substituted bicycloalkadiene" refers to bicycloalkadienes which contain halogen attached to a carbon atom in the ring and/or a side-chain. Thus, both 2-chloromethyl-2,5-norbornadiene and 5-chloromethylene-2-norbornene are halo-substituted bicycloalkadienes.

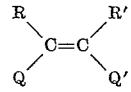
A further object of this invention is to first prepare a haloalkylhalobicycloalkene and then to partially dehydrohalogenate the same to form a halo-substituted bicycloalkadiene.

One embodiment of this invention is found in a process for the preparation of a halo-substituted bicycloalkadiene which comprises condensing a conjugated cycloalkadiene with a haloolefin having the general formula:



in which R is a haloalkyl radical, Q and Q' are radicals selected from the group consisting of hydrogen and halogen radicals, only one of said Q and Q' radicals being halogen, and R' is a radical selected from the group consisting of hydrogen, alkyl, halogen, haloalkyl, cycloalkyl and aryl radicals, thereby forming a haloalkylhalobicycloalkene, and partially dehydrohalogenating said alkene in the presence of a dehydrohalogenating agent selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides, alkali metal alkoxides and amines at a temperature in the range of from about 50° to about 250° C. to form a halo-substituted bicycloalkadiene.

A further embodiment of the invention is found in a process for the preparation of a halo-substituted bicycloheptadiene which comprises condensing cyclopentadiene with a haloolefin having the general formula:



in which R is a haloalkyl radical, Q and Q' are radicals selected from the group consisting of hydrogen and halogen radicals, only one of said Q and Q' radicals being halogen, and R' is a radical selected from the group consisting of hydrogen, alkyl, halogen, haloalkyl, cycloalkyl and aryl radicals, thereby forming a haloalkylhalobicycloheptene, and partially dehydrohalogenating said heptene in the presence of a dehydrohalogenating agent comprising an alkali metal hydroxide and an organic solvent at a temperature in the range of from about 50°

to about 250° C. to form a halo-substituted bicycloheptadiene.

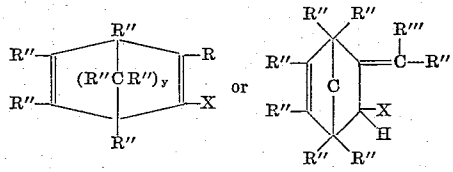
Yet another embodiment of the invention resides in a halogenated 5-alkylidene-2-norbornene.

A specific embodiment of the invention resides in a process for the preparation of a halo-substituted bicycloheptadiene which comprises condensing cyclopentadiene with 2,3-dichloro-1-propene, thereby forming 5-chloro-5-chloromethyl-2-norbornene, and partially dehydrohalogenating said heptene in the presence of potassium hydroxide and ethanol at a temperature in the range of from about 75° to about 200° C. to form 5-chloromethylene-2-norbornene and 2-chloromethyl-2,5-norbornadiene.

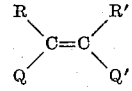
Yet another specific embodiment of the invention is found in 5-chloromethylene-2-norbornene.

Other objects and embodiments referring to alternative reactants utilizable as charging stock in the present process and to alternative dehydrohalogenating agents within the scope of this invention will be referred to in greater detail in the following further detailed description of the invention.

As hereinbefore set forth it has now been discovered that halo-substituted bicycloalkadienes having the following formula:



in which R represents a haloalkyl radical, X represents a hydrogen, halogen, alkyl or haloalkyl radical, y is an integer from 1 to 4, preferably 1 or 2, R″ is independently selected from the group consisting of hydrogen and alkyl radicals and R‴ is a hydrogen, halogen, alkyl or haloalkyl radicals, may be synthesized by condensing, in a Diels-Alder condensation reaction, a conjugated cycloalkadiene with a polyhaloolefin having the general formula:

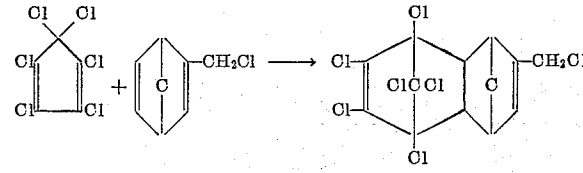


in which R is a haloalkyl radical, R′ is a radical selected from the group consisting of hydrogen, alkyl, halogen, haloalkyl, cycloalkyl and aryl radicals, Q and Q′ are hydrogen or halogen radicals, only one of said Q and Q′ radicals being halogen, to form a haloalkylhalobicycloalkene, and dehydrohalogenating the resultant compound in the presence of a dehydrohalogenating agent, thus yielding new compositions of matter comprising the desired halosubstituted bicycloalkadienes.

The reaction between the conjugated cycloalkadiene and the polyhaloolefin is a thermal condensation of the Diels-Alder type and occurs in the absence of any added catalyst. The condensation usually takes place at a temperature in the range of from about 50° to about 250° C., and preferably in the range of from about 100° to about 200° C. In addition, the reactants are preferably present in a molar ratio range of from about 0.5:1 to about 0.9:1 moles of cycloalkadiene to polyhaloolefin. The excess of polyhaloolefin is preferred in order to insure the production of a bicyclic compound instead of a tetracyclic compound which may occur if the cycloalkadiene is in excess.

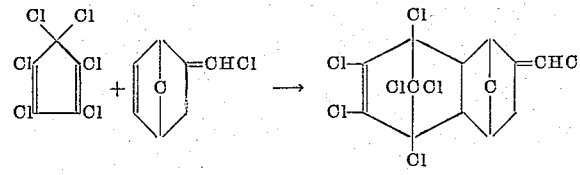
The halo-substituted bicycloalkadienes comprising new compositions of matter which are the desired products of the present invention are useful as intermediates in the preparation of insecticides, pharmaceuticals, resins and plastics. For example, the condensation of a haloalkylbicycloalkadiene such as 2-chloromethyl-2,5-norbornadiene prepared according to the process of this invention, with hexachlorocyclopentadiene yields 1,2,3,4,10,10-hexachloro-6-chloromethyl-1,4,4a,5,8,8a-hexahydro - 1,4,5,8-dimethanonaphthalene.

This reaction is illustrated by the following equation:

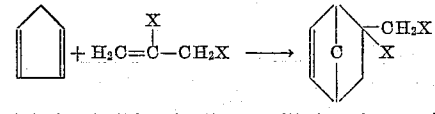


This compound was tested as an insecticide and found to be 100% effective against houseflies when using a 1% concentration and to be 64% effective against houseflies when using a 0.1% concentration. It was also 100% effective against mites (both red spider mites and 2-spotted mites) in an 0.5% concentration.

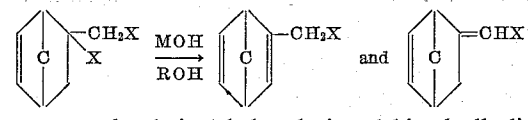
Similarly, the condensation of hexachlorocyclopentadiene with 5-chloromethylene-2-norbornene yields 1,2,3,4,10,10 - hexachloro-6-chloromethylene - 1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-dimethanonaphthalene, which is also an excellent insecticide. This reaction is illustrated by the following equation:



The reaction between the conjugated cycloalkadiene such as cyclopentadiene and a polyhaloolefin such as a 2,3-dihalo-1-propene will proceed according to the following equation:

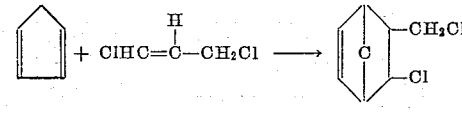


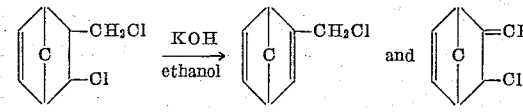
The polyhaloalkylbicycloalkene will then be partially dehydrohalogenated in the presence of a dehydrohalogenating agent such as an alkali metal hydroxide and an organic solvent according to the following equation:



to prepare the desired halo-substituted bicycloalkadiene. In the above equations X represents a halogen, MOH is an alkali metal hydroxide and ROH is an alcohol.

Another, more specific, example of the above method of preparing a halo-substituted bicycloalkadiene is found in the following equations in which cyclopentadiene is reacted with 1,3-dichloro-1-propene and the resulting compound comprising 6-chloro-5-chloromethyl-2-norbornene is dehydrohalogenated in the presence of potassium hydroxide and ethanol to form the desired 2-chloromethyl-2,5-norbornadiene and 6-chloro-5-methylene-2-norbornene.

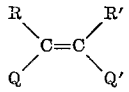




As hereinbefore stated one component of the feed stock is selected from the group of compounds consisting of conjugated cycloalkadienes, such compounds including 1,3-cyclopentadiene (herein referred to as cyclopentadiene), 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,3-cyclooctadiene, etc., alkyl substituted cyclopentadienes such as 1-methylcyclopentadiene, 2-methylcyclopentadiene, 5-methylcyclopentadiene, 5-ethylcyclopentadiene, 5,5-dimethyl-

cyclopentadiene, 1,2-dimethylcyclopentadiene, etc., 1-methyl-1,3-cyclohexadiene, 1 - ethyl-1,3-cyclohexadiene, 1,2-dimethyl-1,3-cyclohexadiene, 1,3-dimethyl-1,3-cyclohexadiene, 1,2-diethyl-1,3-cyclohexadiene, etc. Cyclopentadiene and alkyl substituted cyclopentadienes are preferred reactants in this process due to their relatively greater availability. It is also contemplated within the scope of this invention that dicycloalkadienes which dissociate and become monocycloalkadienes at conditions under which the reaction of this invention proceeds may also be used. Examples of these dicycloalkadienes include dicyclopentadiene, dicyclohexadiene, etc.

The polyhaloolefin compound which as hereinbefore set forth has the general formula:



in which R, R', Q and Q' represent radicals previously set forth, may include

1,3-dichloro-1-propene,
1,3-dibromo-1-propene,
1,3-difluoro-1-propene,
1,3-diiodo-1-propene,
2,3-dichloro-1-propene,
2,3-dibromo-1-propene,
2,3-difluoro-1-propene,
2,3-diiodo-1-propene,
1,3,3-trichloro-1-propene,
1,3,3-tribromo-1-propene,
1,1,3-trichloro-1-propene,
1,1,3-tribromo-1-propene,
1,1,3-trifluoro-1-propene,
1,1,3-triiodo-1-propene,
2,3,3-trichloro-1-propene,
2,3,3-tribromo-1-propene,
2,3,3-trifluoro-1-propene,
2,3,3-triiodo-1-propene,
1,3,3,3-tetrachloro-1-propene,
1,3,3,3-tetrabromo-1-propene,
1,3,3,3-tetrafluoro-1-propene,
1,3,3,3-tetraiodo-1-propene,
2,3,3,3-tetrachloro-1-propene,
2,3,3,3-tetrabromo-1-propene,
2,3,3,3-tetrafluoro-1-propene,
2,3,3,3-tetraiodo-1-propene,
1,4-dichloro-1-butene,
1,4-dibromo-1-butene,
1,4-difluoro-1-butene,
1,4-diiodo-1-butene,
2,4-dichloro-1-butene,
2,4-dibromo-1-butene,
2,4-difluoro-1-butene,
2,4-diiodo-1-butene,
1,4,4-trichloro-1-butene,
1,4,4-tribromo-1-butene,
1,4,4-trifluoro-1-butene,
1,4,4-triiodo-1-butene,
1,4,4,4-tetrachloro-1-butene,
1,4,4,4-tetrabromo-1-butene,
1,4,4,4-tetrafluoro-1-butene,
1,4,4,4-tetraiodo-1-butene,
2,4,4-trichloro-1-butene,
2,4,4-tribromo-1-butene,
2,4,4-trifluoro-1-butene,
2,4,4-triiodo-1-butene,
2,4,4,4-tetrachloro-1-butene,
2,4,4,4-tetrabromo-1-butene,
2,4,4,4-tetrafluoro-1-butene,
2,4,4,4-tetraiodo-1-butene,
1,3-dichloro-2-butene,
1,3-dibromo-2-butene,
1,3-difluoro-2-butene,
1,3-diiodo-2-butene,
1,2-dichloro-2-butene,
1,2-dibromo-2-butene,
1,2-difluoro-2-butene,
1,2-diiodo-2-butene,
1,1,3-trichloro-2-butene,
1,1,3-tribromo-2-butene,
1,1,3-trifluoro-2-butene,
1,1,3-triiodo-2-butene,
1,1,2-trichloro-2-butene,
1,1,2-tribromo-2-butene,
1,1,2-trifluoro-2-butene,
1,1,2-triiodo-2-butene,
1,1,1,3-tetrachloro-2-butene,
1,1,1,3-tetrabromo-2-butene,
1,1,1,3-tetrafluoro-2-butene,
1,1,1,3-tetraiodo-2-butene,
1,1,1,2-tetrachloro-2-butene,
1,1,1,2-tetrabromo-2-butene,
1,1,1,2-tetrafluoro-2-butene,
1,1,1,2-tetraiodo-2-butene,
1-cyclopentyl-2,3-dichloro-1-propene,
1-cyclopentyl-2,3-dibromo-1-propene,
1-cyclopentyl-2,3-difluoro-1-propene,
1-cyclopentyl-2,3-diiodo-1-propene,
1-cyclohexyl-2,3-dichloro-1-propene,
1-cyclohexyl-2,3-dibromo-1-propene,
1-cyclohexyl-2,3-difluoro-1-propene,
1-cyclohexyl-2,3-diiodo-1-propene,
1-phenyl-2,3-dichloro-1-propene,
1-phenyl-2,3-dibromo-1-propene,
1-phenyl-2,3-difluoro-1-propene,
1-phenyl-2,3-diiodo-1-propene,
1-cyclopentyl-2,4-dichloro-1-butene,
1-cyclopentyl-2,4-dibromo-1-butene,
1-cyclopentyl-2,4-difluoro-1-butene,
1-cyclopentyl-2,4-diiodo-1-butene,
1-cyclohexyl-2,4-dichloro-1-butene,
1-cyclohexyl-2,4-dibromo-1-butene,
1-cyclohexyl-2,4-difluoro-1-butene,
1-cyclohexyl-2,4-diiodo-1-butene,
1-phenyl-2,4-dichloro-1-butene,
1-phenyl-2,4-dibromo-1-butene,
1-phenyl-2,4-difluoro-1-butene,
1-phenyl-2,4-diiodo-1-butene, etc.

The dichloropropenes are the preferred polyhaloolefins due to their relatively greater availability and lower cost, and also due to the fact that they will result in the formation of the preferred final products. It is to be understood that the above enumerated conjugated cycloalkadienes and polyhaloolefins of the aforesaid general formula are only representatives of the compounds which may be used, and that this invention is not necessarily limited thereto.

The partial dehydrohalogenation of the polyhaloalkylbicycloalkenes resulting from the reaction between the conjugated cycloalkadiene and the polyhaloolefin is effected by treating said compounds with a dehydrohalogenating agent which includes the hydroxides of the alkali metals and alkaline earth metals such as the hydroxides of lithium, sodium, potassium, rubidium, cesium, calcium, barium, and strontium; amines such as trimethylamine, pyridine, quinoline, etc.; alkali metal alkoxides such as sodium methoxide, potassium ethoxide, etc.; and other basic substances such as potassium carbonate, potassium phenoxide, etc. The hydroxides of the alkali metals and alkaline earth metals may be used as such (fused or powdered) or they may be dissolved in a suitable organic solvent, preferably an alcohol. The particular alcohol which is used as the organic solvent in the dehydrohalogenating reaction will depend largely upon the temperature at which the reaction occurs. Alcohols which are utilizable in this reaction include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, amyl, etc.

The operating conditions under which the process of the present invention is conducted will, to some extent, depend upon the particular compounds employed in the reaction. The temperature for the reaction between the

particular conjugated cycloalkadiene and the polyhaloolefin in which a haloalkylhalobicycloalkene is formed will range from about atmospheric to about 250° C. or more, the preferred range being from about 100° to about 200° C. Likewise, the partial dehydrohalogenation step of this process will also occur at temperatures depending upon the particular reactants and the solvent which is used as a medium for the reaction. Suitable temperatures will usually lie in the range of from about 50° to about 250° C., the preferred range being from 75° to about 200° C. In addition, the reaction will usually take place at atmospheric pressure, however, when the reaction temperature is in a higher range than the boiling point of the solvent, superatmospheric pressures may be employed.

The process of this invention may be effected in any suitable manner and may comprise either a batch or a continuous type operation. When a batch type operation is used, a quantity of the reactants comprising the conjugated cycloalkadiene and the polyhaloolefin is placed in a reactor provided with a mixing and heating device. The reactor is heated to the desired temperature while thoroughly admixing the contents thereof. After a suitable period of time has elapsed, the reactor and its contents are cooled to room temperature, after which the desired product is recovered by suitable means, for example, by fractional distillation or other means known in the art, while the unreacted feed stock may be recharged to form a portion of the starting material of the next batch. The desired product is then placed in a second reactor, or if so desired, returned to the same reactor and the dehydrohalogenating agent and organic solvent added thereto. The reactor is then heated to the desired temperature until the reaction is completed, after which the halo-substituted bicycloalkadiene is separated by suitable means hereinbefore set forth while the organic solvent and dehydrohalogenating agent are recovered for further use in subsequent batches.

Another method of operation of the present process is of the continuous type. In this operation the reactants comprising the conjugated cycloalkadiene and the polyhaloolefin are continuously charged to a reactor provided with heating and mixing means. The reactor may comprise an unpacked vessel or coil or may be lined with an adsorbent packing material such as dehydrated bauxite, alumina and the like, said reactor being maintained at suitable operating conditions of temperature and pressure. The desired reaction product comprising a haloalkylhalobicycloalkene is continuously withdrawn from this vessel by suitable means and charged into a second reactor also maintained at suitable operating conditions, while the unreacted feed stock from the first reactor may be withdrawn and recycled for use as a part of the fresh feed stock. The dehydrohalogenating agent, comprising, for example, an alkali or alkaline earth hydroxide, either in solid or fluidized form or dissolved in the solvent which acts as a medium in which the partial dehydrohalogenation takes place are also charged to the aforesaid second reactor by suitable means. The partially dehydrohalogenated compound, comprising a halo-substituted bicycloalkadiene, is continuously withdrawn from this second reactor and purified by conventional means hereinbefore set forth, while the unreacted material may be recycled to form a portion of the feed stock.

As hereinbefore set forth, the halo-substituted bicycloalkadiene prepared in the above manner may be reacted with a polyhalocycloalkadiene such as hexachyorocyclopentadiene to form polyhaloalkyl tetracyclic compounds which are useful as insecticides. The condensation of the halo-substituted bicycloalkadiene and the hexachlorocyclopentadiene is carried out in a similar manner to the reaction between the conjugated cycloalkadiene and the polyhaloolefin as hereinbefore described. The temperature at which the reaction is to be carried out will be in the range of from about atmospheric to about 250° C. or more, the preferred range being from about 60° to about 200° C. In addition, the reaction may be effected in any suitable manner, either a batch or a continuous type operation similar to that hereinbefore described with reference to the reaction between the cycloalkadiene and the polyhaloolefin. In the batch type operation the reactants comprising the hexachlorocyclopentadiene and the halosubstituted bicycloalkadiene are placed in a reactor provided with heating and mixing devices. This reactor is heated and maintained at the desired temperature until the reaction is completed after which the reactor is cooled to room temperature and the desired reaction product withdrawn, separated and purified by conventional means such as fractional distillation, crystallization, etc.

When a continuous type operation is used the reactants may be introduced into a reactor through lines provided therefor, said reactor being equipped with heating and mixing means and maintained at the desired operating conditions of temperature and pressure. The desired product is withdrawn and purified while the unconverted material may be recycled and used as part of the feed stock, or mixed with fresh starting materials. It is also contemplated within the scope of this invention, that this latter reaction may take place in the presence of inert diluents, e.g. liquid aromatic hydrocarbons such as benzene, toluene, etc.

The physical properties of the insecticides which are prepared by reacting the products of this invention with other organic compounds such as hexachlorocyclopentadiene, the illustrative reactions of said reactions being hereinbefore set forth, and the effects they have on entomological forms of life make them particularly desirable as insecticides and insect repellents, the compounds having many of the features desired of materials for this purpose. They are, for example, toxic to insects which are destructive of plant life and materials normally subject to insect infestation, their toxic effects being manifested by contact of the poison with the insect. The insecticides comprising the present componds are thus effective against chewing as well as sucking types of insects. The compounds are sufficiently volatile so that when applied to plant life intended for subsequent human consumption, the plants when harvested and after allowing a reasonable time for evaporation of the applied insecticide therefrom, retain none of the toxicant to prevent the use of the plant for consumption as food. On the other hand, the compounds are of sufficiently limited volatility to be retained on the insect for the time required to accomplish the toxic effect of the compounds. The volatility and retentive capacity of the compounds may be varied at will by combining them with suitable fixing agents which reduce or promote their volatilization, as desired. Thus, the compounds may be dissolved in a suitable high boiling solvent, such as a mineral or vegetable oil, petroleum, etc.; a wax, such as paraffin wax, beeswax, etc.; a high molecular weight alcohol or ether such as myricyl alcohol, dibutyl ether, etc.; or they may be emulsified with water by the addition of an emulsifying agent, such as a surface active agent, to the mixture of components. The latter solvents and dispersants may also be employed for the specific purpose of reducing the concentration of insecticide to the desired level in a specific insecticidal formulation. The particular formulation of active components in combination with the solvent or dispersant will depend upon its application. Compositions containing as high as 20% of active component may be preferred, in some instances where deep penetration of the insecticide is desired, as in the treatment of fibrous material, such as wood, for extinction of a particular infestation, for example, wood termites. For other purposes the required concentration of active components in the formulation may be as low as 0.1%, as for example, in the treatment of fabrics for destroying moth larvae.

In utilizing the present insecticidal compounds against most insects, a composition containing from about 0.1% to about 5% by weight of the active component is highly effective. The choice of the most desirable solvent or dispersant further depends upon the method utilized to apply the insecticidal composition to the infested article, for example, a low molecular weight, normally gaseous carrying agent. The active insecticidal component, such as propane, butane, the Freons, etc., may be compressed and liquefied into a small bomb containing the insecticide. Upon release of pressure from the bomb, the liquefied carrier vaporizes and suspends a quantity of the active components therein, thus providing a convenient spraying method of applying the insecticide. The active component may also be dissolved in a liquid carrier, such as kerosene, an alcohol, ester, ketone, etc., and the resulting solution atomized by a suitable spraying device.

The present invention is further illustrated with respect to specific embodiments thereof in the following examples which, however, are not intended to limit the generally broad scope of the present invention in strict accordance therewith.

Example I

A mixture of 102 g. of dicyclopentadiene and 200 g. of 2,3-dichloro-1-propene was heated at a temperature in the range of from 180° to 200° C. in a glass liner of a rotating autoclave under 30 atmospheres of initial nitrogen pressure for a period of about 4.5 hours. At the end of this time the liner and contents thereof were cooled to room temperature, the nitrogen vented and the reaction product was separated from unreacted starting materials. The reaction product was subjected to fractional distillation at reduced pressure and the cut boiling at 75–77° C. (at 4 mm. pressure) or 221–223° C. (at 760 mm.) was separated. The cut amounted to 118 g. of 5-chloro-5-chloromethyl-2-norbornene having a refractive index in the range of from 1.5185 to 1.5205.

The 5-chloro-5-chloromethyl-2-norbornene was partially dehydrochlorinated by refluxing 43 g. of product prepared as above described with a solution of 15 g. of potassium hydroxide in n-propyl alcohol at 95° C. for 9 hours. Filtration yielded 9.3 g. of potassium chloride. The filtrate was then distilled, about 120 cc. of overhead boiling at 87–97° C. being obtained, while the temperature of the alcoholic solution rose to 102° C. The solution was refluxed at 102° C. for an additional twelve hours, after which it was cooled and the precipitated potassium chloride (1.2 g.) was filtered off. Water (about 800 cc.) was added to the filtrate as well as to the above-mentioned distillate and the product was extracted with pentane. The pentane extract, which was water washed to remove any dissolved alcohol, was then dried over potassium carbonate and fractionally distilled from potassium carbonate. There was obtained 10 g. of liquid boiling from 89° C. at 52 mm. to 79° C. at 29 mm., converted boiling point: (172–176° C. at 760 mm.); refractive index, n_D^{20}, 1.5157–1.5166. The infrared spectrum of this material indicated that it contained both the cis-ethylenic double bond such as is found in 2-norbornene and a trisubstituted ethylenic double bond exo to the ring. It was apparent that the product consisted chiefly of 5-chloromethylene-2-norbornene mixed with a smaller amount of 2-chloromethyl-2,5-norbornadiene.

Example II

In this experiment the 5-chloro-5-chloromethyl-2-norbornene was prepared in a manner similar to that set forth in Example I above. The 5-chloro-5-chloromethyl-2-norbornene was heated under reflux with an ethyl alcohol solution of potassium hydroxide at 80° C. for a period of approximately 16 hours, after which time the reaction product was separated and subjected to fractional distillation under reduced pressure.

The cut boiling at 69–72°. (at 19 mm. pressure) or 174–175° C. (at 760 mm.) was separated out. This cut, comprising 5-chloromethylene-2-norbornene and 2-chloromethyl-2,5-norbornadiene, having a refractive index of 1.5183 was subjected to analysis. The results of this analysis are set forth below.

Analysis.—Calculated for C_8H_9Cl: C, 68.33; H, 6.45; Cl, 25.22. Found: C, 67.64; H, 6.65; Cl, 25.66.

Example III

A mixture of 102 g. of dicyclopentadiene and 200 g. of 1,3-dichloro-1-propene was heated at a temperature in the range of from about 180° to about 200° C. in a glass liner of a rotating autoclave under 30 atmospheres of initial nitrogen pressure for a period of about 4.5 hours. At the end of this time the liner and contents thereof were cooled to room temperature, the nitrogen was vented and the reaction product comprising 6-chloro-5-chloromethyl-2-norbornene was separated.

A solution of 40 g. of the 6-chloro-5-chloromethyl-2-norbornene and 15 g. of potassium hydroxide in 150 g. of n-propyl alcohol was heated under reflux at 95–98° C. for 9 hours. The potassium chloride which had precipitated (8 g.) was filtered off and the filtrate was distilled to remove about 150 cc. of overhead at 87–96° C. The temperature of the solution rose to 100° C. at which temperature it was refluxed for an additional 11 hours. The product was permitted to cool and was then filtered yielding 4.0 g. additional potassium chloride. The filtrate was combined with the overhead, about 1 liter of water was added and the product was extracted with pentane. The pentane extract was washed with water, dried and distilled from potassium carbonate. There was obtained 11.5 g. of a fraction boiling from 90° C. at 60 mm. to 88° C. at 38 mm., converted boiling point: (169–179° C. at 760 mm.); refractive index, n_D^{20}, 1.5116–1.5130. Infra-red inspection of the product showed that it consisted chiefly of a mixture of 6-chloro-5-methylene-2-norbornene and 2-chloromethyl-2,5-norbornadiene.

Example IV

A mixture of cyclopentadiene and 2,4-dichloro-1-butene is heated at approximately 200° C. in a glass liner of a rotating autoclave under 30 atmospheres under initial nitrogen pressure for a period of time of about 5 hours. At the end of this time, the liner and contents thereof are cooled to room temperature. The nitrogen gas is vented and the reaction product is subjected to fractional distillation under reduced pressure. The cut, comprising 5-chloro-5-(2-chloroethyl)-2-norbornene is separated out.

The above mentioned norbornene is heated under reflux with an ethyl alcohol solution of potassium hydroxide at a temperature of approximately 80° C. for about 16 hours. At the end of this time the reflux vessel and the contents thereof are cooled to room temperature and the reaction product subjected to fractional distillation under reduced pressure. The cut, comprising 5-(2-chloroethylidene)-2-norbornene and 2-(2-chloroethyl)-2,5-norbornadiene is separated and purified by conventional means.

Example V

A mixture of cyclopentadiene and 2,3-dibromo-1-propene is heated at a temperature in the range of from about 180° to about 200° C. in a glass liner of a rotating autoclave under 30 atmospheres of initial nitrogen pressure for a period of time of about 5 hours. At the end of this time the liner and contents thereof are cooled to room temperature, the nitrogen is vented and the reaction product is subjected to fractional distillation under reduced pressure, the cut comprising 5-bromo-5-bromomethyl-2-norbornene being separated out. The aforementioned norbornene is heated under reflux with an ethanol solution of potassium hydroxide at a temperature of approximately 80° C. for a period of about 10 hours. At the end of this time the reflux vessel and contents

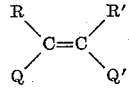
thereof are cooled to room temperature and the reaction product subjected to fractional distillation, the cut comprising 5-bromomethylene-2-norbornene and 2-bromomethyl-2,5-norbornadiene is separated and purified by conventional means.

Example VI

In this example cyclopentadiene and 2,3,3-trichloro-1-propene are condensed in a manner similar to that set forth in the above examples. The reaction product comprising 5-chloro-5-dichloromethyl-2-norbornene is separated and recovered by conventional means hereinbefore described. The aforementioned norbornene is partially dehalogenated by heating under reflux with a propyl alcohol solution of potassium hydroxide at a temperaure of about 85° C. for about 10 hours. At the end of this time the reaction product is subjected to fractional distillation and the cut, comprising 5-dichloromethylene-2-norbornene and 2-dichloromethyl-2,5-norbornadiene is separated and recovered.

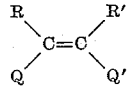
I claim as my invention:

1. A process for the preparation of a halosubstituted bicycloalkadiene which comprises condensing a conjugated cycloalkadiene with a halo-olefin having the general formula



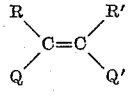
in which R is a haloalkyl radical, Q and Q′ are radicals selected from the group consisting of hydrogen and halogen radicals, only one of said Q and Q′ radicals being halogen, and R′ is a radical selected from the group consisting of hydrogen, alkyl, halogen, haloalkyl, cycloalkyl and aryl radicals, thereby forming a haloalkylhalobicycloalkene, and partially dehydrohalogenating said alkene in the persence of a dehydrohalogenating agent selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides, alkali metal alkoxides and amines at a temperaure in the range of from about 50° to about 250° C. to form a halo-substituted bicycloalkadiene.

2. A process for the preparation of a halo-substituted bicycloalkadiene which comprises condensing a conjugated cycloalkadiene with a halo-olefin having the general formula



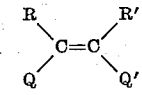
in which R is a haloalkyl radical, Q and Q′ are selected from the group consisting of hydrogen and halogen radicals, only one of said Q and Q′ radicals being halogen, and R′ is a radical selected from the group consisting of hydrogen, alkyl, halogen, haloalkyl, cycloalkyl and aryl radicals, thereby forming a haloalkylhalobicycloalkene, and partially dehydrohalogenating said alkene in the presence of a dehydrohalogenating agent comprising an alkali metal hydroxide and an organic solvent at a temperature in the range of from about 50° to about 250° C. to form a halo-substituted bicycloalkadiene.

3. A process for the preparation of a halo-substituted bicycloalkadiene which comprises condensing a conjugated cycloalkadiene with a halo-olefin having the general formula



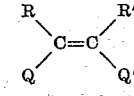
in which R is a haloalkyl radical, Q and Q′ are selected from the group consisting of hydrogen and halogen radicals, only one of said Q and Q′ radicals being halogen, and R′ is a radical selected from the group consisting of hydrogen, alkyl, halogen, haloalkyl, cycloalkyl and aryl radicals, thereby forming a haloalkylhalobicycloalkene, and partially dehydrohalogenating said alkene in the presence of a dehydrohalogenating agent comprising potassium hydroxide and alcohol at a temperature in the range of from about 50° to about 250° C. to form a halo-substituted bicycloalkadiene.

4. A process for the preparation of a halo-substituted bicycloalkadiene which comprises condensing a conjugated cycloalkadiene with a halo-olefin having the general formula



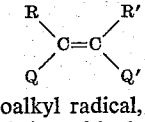
in which R is a haloalkyl radical, Q and Q′ are selected from the group consisting of hydrogen and halogen radicals, only one of said Q and Q′ radicals being halogen, and R′ is a radical selected from the group consisting of hydrogen, alkyl, halogen, haloalkyl, cycloalkyl and aryl radicals, thereby forming a haloalkylhalobicycloalkene, and partially dehydrohalogenating said alkene in the presence of a dehydrohalogenating agent comprising potassium hydroxide and ethanol at a temperature in the range of from about 50° to about 250° C. to form a halo-substituted bicycloalkadiene.

5. A process for the preparation of a halo-substituted bicycloalkadiene which comprises condensing a conjugated cycloalkadiene with a halo-olefin having the general formula



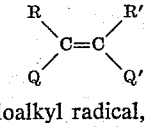
in which R is a haloalkyl radical, Q and Q′ are selected from the group consisting of hydrogen and halogen radicals, only one of said Q and Q′ radicals being halogen, and R′ is a radical selected from the group consisting of hydrogen, alkyl, halogen, haloalkyl, cycloalkyl and aryl radicals, thereby forming a haloalkylhalobicycloalkene, and partially dehydrohalogenating said alkene in the presence of a dehydrohalogenating agent comprising potassium hydroxide and a propyl alcohol at a temperature in the range of from about 50° to about 250° C. to form a halo-substituted bicycloalkadiene.

6. A process for the preparation of a halo-substituted bicycloalkadiene which comprises condensing a conjugated cycloalkadiene with a halo-olefin having the general formula



in which R is a haloalkyl radical, Q and Q′ are selected from the group consisting of hydrogen and halogen radicals, only one of said Q and Q′ radicals being halogen, and R′ is a radical selected from the group consisting of hydrogen, alkyl, halogen, haloalkyl, cycloalkyl and aryl radicals, thereby forming a haloalkylhalobicycloalkene, and partially dehydrohalogenating said alkene in the presence of a dehydrohalogenating agent comprising sodium hydroxide and ethanol at a temperature in the range of from about 50° to about 250° C. to form a halo-substituted bicycloalkadiene.

7. A process for the preparation of a halo-substituted bicycloheptadiene which comprises condensing cyclopentadiene with a halo-olefin having the general formula



in which R is a haloalkyl radical, Q and Q′ are radicals selected from the group consisting of hydrogen and halogen radicals, only one of said Q and Q′ radicals being halogen, and R′ is a radical selected from the group consisting of hydrogen, alkyl, halogen, haloalkyl, cycloalkyl and aryl radicals, thereby forming a haloalkylhalobicyclo-

heptene, and partially dehydrohalogenating said heptene in the presence of a dehydrohalogenating agent comprising an alkali metal hydroxide and an organic solvent at a temperature in the range of from about 50° to about 250° C. to form a halo-substituted bicycloheptadiene.

8. A process for the preparation of a halo-substituted bicycloheptadiene which comprises condensing cyclopentadiene with 2,3-dichloro-1-propene, thereby forming 5-chloro-5-chloromethyl-2-norbornene, and partially dehydrohalogenating said heptene in the presence of potassium hydroxide and ethanol at a temperature in the range of from about 75° to about 200° C. to form 5-chloromethylene-2-norbornene and 2-chloromethyl-2,5-norbornadiene.

9. A process for the preparation of a halo-substituted bicycloheptadiene which comprises condensing cyclopentadiene with 2,3-dibromo-1-propene, thereby forming 5-bromo-5-bromomethyl-2-norbornene, and partially dehydrohalogenating said heptene in the presence of potassium hydroxide and ethanol at a temperature in the range of from about 75° to about 200° C. to form 5-bromomethylene-2-norbornene and 2-bromo-2,5-norbornadiene.

10. A process for the preparation of a halo-substituted bicycloheptadiene which comprises condensing cyclopentadiene with 1,3-dichloro-1-propene, thereby forming 5-chloro-6-chloromethyl-2-norbornene, and partially dehydrohalogenating said norbornene with potassium hydroxide and ethanol at a temperature in the range of from about 75° to about 200° C. to form 6-chloro-5-methylene-2-norbornene and 2-chloromethyl-2,5-norbornadiene.

11. A process for the preparation of a halo-substituted bicycloheptadiene which comprises condensing 2,3,3-trichloro-1-propene with cyclopentadiene, thereby forming 5-chloro-5-dichloromethyl-2-norbornene, and partially dehydrohalogenating said norbornene with potassium hydroxide and propanol at a temperature in the range of from about 75° to about 200° C. to form 5-dichloromethylene-2-norbornene and 2-dichloromethyl-2,5-norbornadiene.

12. A process for the preparation of a halo-substituted bicycloheptadiene which comprises condensing 2,4-dichloro-1-butene with cyclopentadiene, thereby forming 5-chloro-5-(2-chloroethyl)-2-norbornene, and partially dehydrohalogenating said norbornene in the presence of potassium hydroxide and ethanol at a temperature in the range of from about 75° to about 200° C. to form 5-(2-chloroethylidene-2-norbornene and 2-(2-chloroethyl)-2,5-norbornadiene.

13. A 5-haloalkylidene-2-norbornene.

14. 5-chloromethylene-2-norbornene.

15. 5-bromomethylene-2-norbornene.

16. 6-chloro-5-methylene-2-norbornene.

17. 5-dichloromethylene-2-norbornene.

18. 5-(2-chloroethylidene)-2-norbornene.

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