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3,258,501

PRODUCTION OF POLYCYCLIC COMPOUNDS

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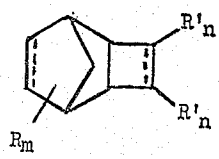
No Drawing. Filed Mar. 30, 1964, Ser. No. 355,889
6 Claims. (Cl. 260—666)

This invention relates to a novel class of polycyclic organic compounds and to methods for the production thereof. More particularly, it relates to novel saturated and ethylenically unsaturated tricyclo(4.2.1.$0^{2,5}$) hydrocarbons containing a ring system of 9 carbon atoms, and the methods by which such polycyclic compounds are produced.

It is an object of the present invention to provide a novel class of polycarbocyclic organic compounds and methods for the production thereof. More particularly, it is an object of the present invention to prepare novel hydrocarbons containing a tricyclo(4.2.1.$0^{2,5}$) carbocyclic ring system, which ring system is saturated or contains from 1 to 2 ethylenic linkages wherein no bridgehead carbon atom is a member of an ethylenic carbon-carbon bond. An additional object is to provide novel methods for the production of such tricyclic compounds.

It has now been found that these objects are accomplished by processes which comprise the condensation of unsaturated bicyclic ring systems with certain other unsaturated molecules in the presence of transition metal complexes as catalysts. Such condensation processes provide the desired ring system directly, or alternatively provide precursors thereof, from which compounds incorporating the desired ring system are easily obtained.

The novel compounds of the invention comprise the tricyclo(4.2.1.$0^{2,5}$)nonanes and the corresponding ethylenically unsaturated tricyclic compounds having from 1 to 2 endo ethylenic linkages, i.e., non-aromatic carbon-carbon double bonds, wherein both carbon atoms are members of the carbocyclic ring system. Generically, these compounds are non- to di-ethylenically unsaturated tricyclo(4.2.1.$0^{2,5}$)nonanes. Although numerous position isomers are available when the tricyclic compound contains ethylenic linkage(s), preferred compounds of the invention are those non- to di-ethylenically unsaturated tricyclo(4.2.1.$0^{2,5}$)nonanes wherein no bridgehead carbon atom, i.e., no carbon atom common to two or more rings, is a member of an ethylenic linkage. One class of such compounds has from 9 to 89 carbon atoms, preferably from 9 to 40, and is represented by the formula



wherein R and R′ independently are hydrocarbon containing no nonaromatic unsaturation, e.g., alkyl, cycloalkyl and aryl, having from 1 to 10 carbon atoms, preferably from 1 to 6; *m* represents the number of R groups and is a whole number from 0 to 6 inclusive and *n* is a whole number from 0 to 1 inclusive representing the number of R′ groups. In the above-depicted formula, the dotted line designation is employed to indicate possible locations of ethylenic linkages. The designation, as employed herein, generically signifies that the bond between the carbon atoms connected by the dotted line may be a single bond, i.e., a saturated carbon-carbon linkage, or alternatively may be a double bond, i.e., an ethylenic linkage, depending, of course, on whether the polycyclic compound is saturated, mono-ethylenically unsaturated or di-ethylenically unsaturated. It will be appreciated that in accord with the preference for tricyclic compounds which are saturated or unsaturated with endo ethylenic linkages not involving bridgehead carbon atoms, the locations designated by the dotted lines are the only carbon-carbon bonds which may alternatively be single or double bonds depending upon the degree of ethylenic unsaturation in the molecule. It should be understood that in the above-depicted formula, R and R′ groups replace hydrogen substituents on the corresponding unsubstituted non- to di-ethylenically unsaturated tricyclo(4.2.1.$0^{2,5}$)-nonane. Preferred compounds of the above-depicted formula have only a single substituent on any one carbon atom of the eight-membered ring, and most preferred are the compounds wherein the 2 and 5 carbon atoms possess hydrogen substituents.

The tricyclic compounds of the invention are produced by alternate methods. Each method, however, involves the condensation of a bicyclic compound with an unsaturated molecule in the presence of a transition metal complex as catalyst. Suitable catalysts are complexes of transition metals of Group VIII of the Periodic Table, particularly nickel, wherein the metal is present in a reduced oxidation state and is complexed with stabilizing ligands. By stabilizing ligand is meant a ligand capable of donating an electron pair to form a coordinate bond with the metal, and simultaneously having the ability to accept electrons from the metal, thereby imparting stability to the resulting complex. Examples of such stabilizing ligands are carbon monoxide; compounds containing conjugated unsaturation such as acrylonitrile, methyl vinyl ketone and acrolein; cyclic polyolefins such as 1,5-cyclooctadiene and bicyclo(2.2.1)hepta-2,5-diene; acetylenes such as 2-butyne and phenylacetylene; trisubstituted derivatives of trivalent members of Group V of the Periodic Table, such as the phosphines, phosphites, stibines and arsines; and the like. Suitable nickel complex catalysts are those wherein the nickel is present in a reduced oxidation state, e.g., +1 or lower, and preferred catalysts contain nickel in a zero oxidation state complexed with stabilizing ligands. Although nickel complexes such as tetrakis(trialkylphosphine)nickel (0), tetrakis(triarylarsine)nickel (0), tetrakis(triarylphosphine)nickel (0) and bis(trialkylstibine)nickel (0) dicarbonyl are satisfactory, best results are obtained when the catalyst is a tetrakis(trihydrocarbylphosphite)nickel (0) complex. Such catalysts are represented by the formula $[P(OR'')_3]_4Ni$ wherein R″ independently is hydrocarbyl having from 1 to 10 carbon atoms, as illustrated by alkyl R″ groups such as methyl, ethyl, propyl, sec-butyl, amyl, iso-amyl, hexyl, octyl, 2-ethylhexyl, decyl, benzyl and β-phenylethyl; cycloalkyl R″ groups including cyclopentyl and cyclohexyl; and aryl R″ groups such as phenyl, tolyl, xylyl, ethylphenyl and p-tert-butylphenyl. Preferred R″ groups are free from non-aromatic unsaturation, and in general, acyclic alkyl groups are preferred over cycloalkyl and aryl substituents in the phosphite ligands of the catalyst.

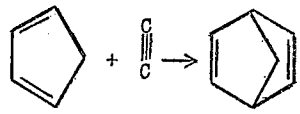
Exemplary tetrakis(trihydrocarbylphosphite)nickel (0) 10 catalysts include

Tetrakis(tributylphosphite)nickel (0),
Tetrakis(triphenylphosphite)nickel (0),
Tetrakis(tripropylphosphite)nickel (0),
Bis(tritolylphosphite)bis(trihexylphosphite)nickel (0),
Tetrakis(amyldibutylphosphite)nickel (0)

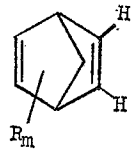
and the like. Particularly useful as catalyst is tetrakis[tri-(2-ethylhexyl)phosphite]nickel (0). The nickel (0) catalysts are conveniently prepared by any of several methods, e.g., according to the disclosure of U.S. 3,102,899 issued September 3, 1963, to Cannell, or the disclosure of copending application of Mullineaux, Serial No. 275,517, filed April 25, 1963.

The nickel (0) complex catalysts are preferably employed as preformed materials but alternatively may be prepared in situ, as by the reaction of a nickel (I) or nickel (II) compound with a suitable reducing agent. For example, nickel (II) acetylacetonate reacts with triethyl aluminum in the presence of triphenylphosphine and the reactants at temperatures from about —20° C. to about 20° C. to afford a nickel (0) catalyst.

In one modification of the process of the invention, the tricyclic compounds are produced by the dimerization of a bicyclo(2.2.1)hepta-2,5-diene in the presence of the preferred nickel (0) complex catalyst, followed by pyrolysis of the product thereby produced. The bicyclo(2.2.1)-hepta-2,5-diene is conveniently prepared from a cyclopentadiene and an acetylene such as by the process described in U.S. 2,875,256 issued February 24, 1959, to Hyman et al.

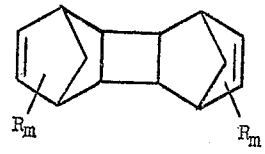


By the choice of appropriately substituted cyclopentadienes and acetylenes, bicyclo(2.2.1)hepta-2,5-dienes containing varied substituents may be produced, for example, from 2,3-dimethylcyclopentadiene and acetylene is produced 2,3 - dimethylbicyclo(2.2.1)hepta - 2,5-diene. Preferred bicyclo(2.2.1)hepta-2,5-dienes are those wherein any ring substituents are hydrocarbyl, and from consideration of subsequent process steps, it is preferred that at least one pair of carbon atoms connected by an ethylenic linkage have hydrogen substituents. Such preferred bicycloheptadienes are represented by the formula

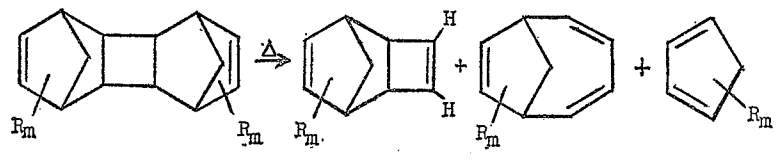


wherein R and *m* have the previously stated significance. The bicycloheptadienes are dimerized by heating the bicycloheptadiene in the presence of a catalytic amount of the nickel (0) complex catalyst previously characterized. This process is described more fully in co-pending application of Muller et al., Serial No. 257,090, filed February 8, 1963.

The products of bicycloheptadiene dimerization are pentacyclo(8.2.1.1^{4,7}.0^{2,9}.0^{3,8})tetradeca-5,11-dienes. When the preferred bicycloheptadiene reactants are employed, the dimer products are represented by the formula



wherein R and *m* have the previously stated significance. Subsequent to the dimerization process, the pentacyclotetradecadienes are thermally converted to a reaction mixture containing the desired tricyclononadiene, a bicyclononatriene byproduct that is isomeric therewith, and cyclopentadiene in an amount equimolar with the total of the polycyclic compounds. This conversion is illustrated by the equation below wherein R and *m* have the previously stated significance.



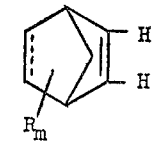
The thermal conversion of pyrolysis of the pentacyclotetradecadiene is conducted in a batchwise manner, as by maintaining the reactant at an elevated temperature and removing the pyrolysis products therefrom as by distillation, or alternatively the pyrolysis is conducted in a continuous manner as by passing the pentacyclotetradecadiene through a heated tube and recovering the desired product from the effluent. It will be appreciated that although the above formula represents a planar configuration, various endo and exo isomers of the pentacyclotetradecadiene are formed during bicycloheptadiene dimerization and the ease of pyrolysis of the isomers will be somewhat variable. Pyrolysis temperatures above about 200° C. are generally satisfactory, although it is desirable to avoid pyrolysis temperatures above about 525° C., in part because of the significant amounts of byproducts, e.g., allylbenzene and indene, obtained by the rearrangement of the polycyclic reactant when such higher temperatures are employed. Best results are obtained when pyrolysis temperatures from about 250° C. to about 450° C. are utilized. The pyrolysis may be conducted at pressures that are atmospheric, subatmospheric or superatmospheric. Little advantage is gained by the use of pressures other than atmospheric, and utilization of pressures that are substantially atmospheric is preferred.

The ratio of the polycyclic products obtained by pyrolysis is somewhat determined by the reaction conditions, particularly the pyrolysis temperature and the residence time, that are employed. At reaction temperatures below about 300° C., the molar ratio of tricyclononadiene to bicyclononatriene is about 7:1. At higher temperatures, the relative proportion of bicyclotriene increases, probably because of isomerization of the tricyclononadiene under the more vigorous conditions. The production of bicyclo(4.2.1)nona-2,4,7-triene and derivatives thereof is described more fully and is claimed in co-pending application of L. G. Cannell, filed of even date.

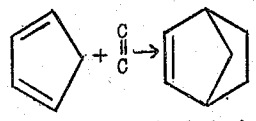
Subsequent to the pyrolysis reaction, the products are separated and recovered by conventional methods such as fractional distillation, selective extraction and the like.

An alternate method for the production of the novel tricyclic compounds of the invention comprises the reaction of a mono- to di-ethylenically unsaturated bicyclo(2.2.1)heptane with an acetylenic hydrocarbon in the presence of the nickel (0) complex as catalyst. The acetylenic hydrocarbon comprises a carbon-carbon triple bond wherein the carbon atoms thereof are substituted with hydrogen or hydrocarbyl radicals which contain no nonaromatic unsaturation. Preferred acetylenic hydrocarbons are represented by the formula $R'_n—C\equiv R'_n$ wherein R' and *n* have the previously stated significance. It will be understood that when either *n* is 0, the remaining valence of the carbon atom(s) will be completed by combination with hydrogen atom(s). The acetylenic hydrocarbons are mono-alkynes having from 2 to 22 carbon atoms, preferably from 2 to 14.

The acetylenic hydrocarbon is reacted with a mono- to di-ethylenically unsaturated bicyclo(2.2.1)heptane wherein no bridgehead carbon atom is a member of an ethylenic linkage, and wherein the carbon atoms of at least one ethylenic linkage is substituted with hydrogens. Preferred reactants are generically represented by the formula



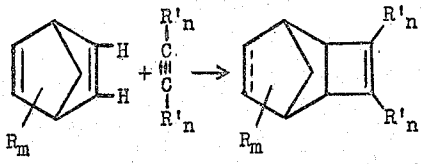
wherein R, *m* and the dotted line designation have the previously stated significance. The bicyclo(2.2.1)hepta-2,5-dienes are produced as hereinbefore described by condensation of a cyclopentadiene and an acetylene. In like manner, bicyclo(2.2.1)hept-2-enes are produced from conventional condensation of cyclopentadienes and ethylenic compounds as illustrated by the following equation.



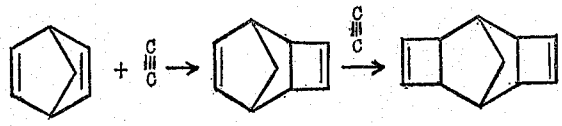
The reaction of mono- to di-ethylenically unsaturated bicyclo(2.2.1)heptane and the acetylenic hydrocarbon is effected by mixing the reactants and nickel (0) complex catalyst and maintaining the mixture at a somewhat elevated reaction temperature until reaction is complete. Reaction temperatures from about 30° C. to about 250° C. are satisfactory, although reaction temperatures from about 100° C. to about 200° C. are preferred. While the condensation may be conducted at atmospheric pressure, it is generally desirable to employ pressures that are superatmospheric. Suitable reaction pressures vary from about 1 to about 100 atmospheres. Particular advantage is taken of the pressures generated when the reaction mixture is heated to reaction temperature in a sealed vessel, which pressures typically vary from about 2 to about 20 atmospheres.

The nickel complex is employed in catalytic amounts. Amounts of nickel complex catalyst from about 0.001% mole to about 5% mole based upon the limiting reactant are suitable, although amounts of catalyst from about 0.01% mole to about 1% mole on the same basis are preferred.

The reaction of mono- to di-ethylenically unsaturated bicyclo(2.2.1)heptane with acetylenic hydrocarbon results in the formation of mono- to di-ethylenically unsaturated tricyclo(4.2.1.$0^{2,5}$)nonanes. The reaction is illustrated by the equation

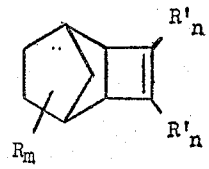


wherein R, R′, *m*, *n* and the dotted line designation have the previously stated significance. A somewhat special case exists when a bicyclo(2.2.1)hepta-2,5-diene is employed as the reactant, as the presence of two ethylenic linkages allows successive condensations with two molecules of acetylenic hydrocarbon to produce a quadricyclo (4.4.1.$0^{2,5}$.$0^{7,10}$)undeca-3,8-diene, in addition to the tricyclo(4.2.1.$0^{2,5}$)nona-3,7-diene.



The formation of the quadricyclic compound is favored by utilization of higher reaction temperatures and an excess amount of acetylenic hydrocarbon relative to the amount of bicycloheptadiene, e.g., a molar ratio of at least 2:1. Such quadricycloundecadienes, although also novel, are generally less preferred than the analogous tricyclononadienes, and in the reaction of bicycloheptadienes with acetylenic hydrocarbon, as well as in the reaction of bicycloheptenes, it is preferred to employ amounts of reactants that are substantially equimolar. A molar excess of the bicyclic reactant or a molar excess of acetylenic hydrocarbon when bicycloheptenes are employed does not appear to be detrimental, although little advantage is gained by utilization of such excesses and the use of substantially stoichiometric quantities of reactants is preferred.

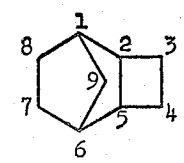
The quadricyclo(4.4.1.$0^{2,5}$.$0^{7,10}$)undeca-3,8-diene is representative of a class of compounds which, although less preferred, is within the contemplated scope of the invention because of the presence within the molecule of the tricyclo(4.2.1.$0^{2,5}$)non-3-ene ring system. Such compounds are represented by the formula



wherein R, R′, *m* and *n* have the previously stated significance, with the proviso that R substituents on the 7 and 8 carbon atoms may together with the 7 and 8 carbon atoms form a carbocyclic ring system, preferably monocyclic, of from 4 to 7 carbon atoms, especially a cyclobutane or a cyclobutene ring. An additional example of this class of compounds is quadricyclo(4.4.1.$0^{2,5}$.$0^{7,10}$) undecane formed by hydrogenation of the quadricycloundecadiene by methods described hereinafter.

Regardless of the method of production, the mono- to di-ethylenically unsaturated tricyclo(4.2.1.$0^{2,5}$)nonanes are suitable for conversion to the corresponding saturated compounds or compounds containing a lesser degree of unsaturation by processes of hydrogenation. For example, tricyclo(4.2.1.$0^{2,5}$)nona-3,7-dienes are converted to a mixture of partially saturated derivatives, e.g., a mixture of tricyclo(4.2.1.$0^{2,5}$)non-3-ene and tricyclo(4.2.1.$0^{2,5}$)non-7-ene, by partial hydrogenation. Such a mixture is separated by conventional methods, e.g., distillation. By processes of complete hydrogenation, for example by allowing hydrogenation to proceed to completion, the nonadiene or either of the isomeric nonenes are converted to tricyclo(4.2.1.$0^{2,5}$)nonanes. Hydrogenation is conveniently accomplished by contacting the unsaturated tricyclic compounds with molecular hydrogen in the presence of a conventional hydrogenation catalyst. Illustrative of such catalysts are transition metals of Group VIII of the Periodic Table, e.g., nickel, platinum, palladium and rhodium or oxides thereof, which may be unsupported or supported on such inert carriers as carbon, alumina and the like, as well as mixed oxide catalyst, e.g., copper chromite.

It is apparent from the above discussion that the processes of the invention may be employed to produce a variety of saturated and unsaturated tricyclic compounds. The products of the invention, as well as the reactants from which they are produced, are named in accord with conventional systems of naming and numbering polycyclic compounds. The tricyclononanes, for example, are numbered according to the following system.



Typical of the products of the invention, numbered in this manner, are

Tricyclo(4.2.1.$0^{2,5}$)nonane,
Tricyclo(4.2.1.$0^{2,5}$)nona-3,7-diene,
3,4-dimethyltetracyclo(4.2.1.$0^{2,5}$)non-3-ene,
7,8-diphenyltricyclo(4.2.1.$0^{2,5}$)nonane,
3,4,7,8-tetraphenyltricyclo(4.2.1.$0^{2,5}$)non-7-ene,
3-butyl-1-methyltricyclo(4.2.1.$0^{2,5}$)nona-3,7-diene,
9,9-dimethyltricyclo(4.2.1.$0^{2,5}$)non-3-ene,
7-benzyltricyclo(4.2.1.$0^{2,5}$)non-7-ene,
1,3,4-trimethyltricyclo(4.2.$0^{2,5}$)nona-3,7-diene
and the like.

The novel ring-unsaturated compounds are useful in a variety of applications as chemical intermediates. By employing the ethylenic unsaturation as reactive sites, the compounds of the invention may be polymerized or co-polymerized with reactive unsaturates to form elastomers and thermoplastics. They are useful as ligands in the production of metal complexes, as dienophiles in Diels-Alder condensations with many dienes, and additionally may be epoxidized to form useful epoxy resin precursors. The unsaturated linkages may be hydrated or hydroxylated to form novel alcohols from which many useful conventional derivatives may be produced. The saturated tricyclo(4.2.1.$0^{2,5}$)nonanes of the invention find application as special solvents, e.g., in the field of coatings, and are also useful as components of high energy fuels.

To further illustrate the novel processes of the invention and the novel products obtained thereby, the following examples are provided. It should be understood that they are not to be regarded as limitations, as the teachings thereof may be varied as will be understood by one skilled in this art.

Example I

Pentacyclo(8.2.1.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$)tetradeca-5.11 - diene (bicycloheptadiene dimer), 20 g., was placed in a round-bottomed flask equipped with an 8 cm. vacuum-jacketed reflux column having a water-cooled take-off condenser and an ice bath-cooled receiver. The contents of the flask were maintained at 260–270° C. by heating in an oil bath. As the dimer refluxed slowly, the pyrolysis products distilled from the reaction mixture and were collected in the receiver. When 9.8 g. of product had been collected, the product mixture was analyzed and found to contain 34.9% cyclopentadiene, 56.8% tricyclo(4.2.1.$0^{2,5}$) nona-3,7-diene, 7.3% bicyclo(4.2.1)nona-2,4,7-triene and 1% recovered bicycloheptadiene dimer, all percentages being by weight. Distillation of the product mixture afforded separation of the tricyclo(4.2.1.$0^{2,5}$)nona-3,7-diene, B.P. 78.5° C. at 106 mm., n_D^{20} 1.4998, as a colorless liquid.

Analysis.—Calc.: C, percent wt. 91.47; H, percent wt. 8.53. Found: C, percent wt. 91.49; H, percent wt. 8.57.

Mass spectroscopy indicated the product had a molecular weight of 118, and the nuclear magnetic resonance spectrum was consistent with the above formula.

Example II

Pentacyclo(8.2.1.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$)tetradeca-5,11-diene (bicycloheptadiene dimer) was introduced at a constant rate along with helium as a carrier gas, into a heated glass tube. A total of 7.4 g. of the dimer were introduced over a period of 70 minutes to a tube heated to 400° C. The residence time in the tube was 0.16 minute. A liquid product was obtained, 7.2 g., which was shown by gas-liquid chromatographic analysis to contain 6.1 millimole of tricyclo(4.2.1.$0^{2,5}$)non-3,7-diene, 26.7 millimoles of bicyclo(4.2.1)nona-2,4,7-triene, 31.6 millimoles of cyclopentadiene and 6.6 millimoles recovered feed.

Example III

Into an 84 ml. autoclave was introduced, under nitrogen, 16.7 g. of bicyclo(2.2.1)-2-heptene, 16.7 g. of 2-butyne and 1.0 g. of tetrakis[tri(2-ethylhexyl)phosphite] nickel (0) as catalyst. The resulting mixture was heated at 180–185° C. for 10 hours, during which time the pressure dropped from 190 p.s.i.g. to 40 p.s.i.g. Separation and gas-liquid chromatographic analysis of the 35.0 g. of liquid product indicated the presence of 6.81 g. unreacted 2-butyne, 2.49 g. of bicycloheptadiene, 16.22 g. of 3,4-dimethyltricyclo(4.2.1.$0^{2,5}$)non-3-ene and 8.39 g. of unidentified products. The products were obtained by fractional distillation, subsequent to removal of unreacted cyclopentadiene by distillation under reduced pressure at ambient temperature, thereby preventing cyclopentadiene dimerization. The novel dimethyltricyclonene, n_D^{20} 1.4836, distilled at 110° C. at 100 mm. A mass spectrogram of this product showed a molecular weight of 148, and the nuclear magnetic resonance spectrum was consistent with the above formula.

Example IV

Into an 84 ml. autoclave was introduced, under nitrogen, 39.0 g. of bicyclo(2.2.1)hepta-2,5-diene, 15.0 g. of diphenylacetylene and 1.0 g. of tetrakis[tri(2-ethylhexyl) phosphite]nickel (0). The reaction mixture was heated at 100° C. for 0.8 hour and at 120° C. for 2 additional hours. The product mixture was analyzed by gas-liquid chromatography and separated by distillation to give 16.9 g. of a viscous, colorless liquid, B.P. 172–3° C. at 2.6 mm., which represented a yield of 74%. The product, 3,4-diphenyltricyclo(4.2.1.$0^{2,5}$)nona-3,7-diene, was shown to have a molecular weight of 270, and the nuclear magnetic resonance spectrum was consistent with a mixture of the endo and exo isomers of the above formula.

Example V

A mixture of 10 g. of 2-butyne and 17 g. of bicyclo (2.2.1)hepta-2,5-diene were placed in an 84 ml. autoclave which was equipped with a magnetic stirrer. After 1 g. of tetrakis[tri(2-ethylhexyl)phosphite]nickel(0) was added, the mixture was heated at 160–70° C. for 3.5 hours while the reaction mixture was stirred. The reaction product mixture was analyzed by gas-liquid chromatography and separated by distillation under reduced pressure.

The product mixture contained 16.6 g. of 3,4-dimethyl tricyclo(4.2.1.$0^{2,5}$)nona-3,7-diene, a 1:1 addition product, 2.0 g. of 1,2,3,4-tetramethylbenzene and 1.1 g. of 3,4,8,9-tetramethylquadricyclo(4.4.1.$0^{2,5}$.$0^{7,10}$)undeca-3,8-diene, a product arising from condensation of the acetylene and the bicycloheptadiene in a 2:1 ratio. A mass spectrogram of the tricyclononadiene indicated a molecular weight of 146, and the nuclear magnetic resonance spectrum was consistent with a mixture of exo and endo isomers of the above formula.

Example VI

The procedure of Example V was followed to react 20 g. of 2-butyne with 15 g. of bicyclo(2.2.1)hepta-2,5-diene in the presence of 1.5 g. of the same nickel catalyst at a temperature of 180–3° C. for 107 minutes and an additional 37 minutes at 200° C. The recovered liquid product, 34.8 g. consisted of 20.7 g. of 3,4,8,9-tetramethylquadricyclo(4.4.1.$0^{2,5}$.$0^{7,10}$)undeca-3,8-diene, 2.1 g. of 1,2,3,4-tetramethylbenzene, 1.2 g. of hexamethylbenzene, 0.9 g. of unreacted 2-butyne and 9.9 g. of unidentified products, and a trace of 3,4-dimethyltricyclo(4.2.1.$0^{2,5}$) nona-3,7-diene.

The tetramethylquadricycloundecadiene, n_D^{25} 1.5000–1.5020, distilled at 103° C. at 8.5 mm. A mass spectrogram showed the molecular weight to be 200, a $c_{15}H_{20}$ compound, corresponding to a 2:1 condensation product of 2-butyne and bicycloheptadiene. The nuclear magnetic resonance spectrum was consistent with a mixture of exo and endo isomers of the above formula.

Example VII

Under a variety of reaction conditions, 1-butyne was reacted with bicyclo(2.2.1)hepta-2,5-diene in the presence of nickel (0) catalysts. The reaction conditions, and the yield of 3-ethyltricyclo(4.2.1.$0^{2,5}$)nona-3,7-diene are shown in Table 1.

TABLE 1

Catalyst	$[(C_6H_5O)_2POCH_2]_{2+2}Ni$	$[(2\text{-ethylhexyl-O})_3P]_4Ni$		
Feed, g.:				
1-butyne	8	19	15	10
Bicycloheptadiene	20.0	15.0	15.0	15.0
Catalyst	1.0	1.5	1.0	1.0
Reaction Conditions, ° C./min.	153–60°/300	100–80/20 and 180/360.	100–70/30 and 170–77/270.	120–30/156
Recovered Feed:				
1-butyne	3.7	2.5	4.8	5.8
Bicycloheptadiene	15.9	1.7	6.3	9.4
Product, g.:				
Ethyl tricyclononadiene	3.2	5.7	3.3	1.2
Diethylbenzenes	1.6	11.4	6.8	3.0

Example VIII

In an 84 ml. autoclave, 5.96 g. of tricyclo(4.2.1.$0^{2,5}$)nona-3,7-diene, B.P. 86° C. at 150 mm., n_D^{20} 1.5003, was hydrogenated at 50° C. and an initial pressure of 830 p.s.i.g., using 0.2% Pd-on-charcoal catalyst. The hydrogen uptake was 0.105 millimole; theoretical uptake is 0.101 millimole. The product, tricyclo(4.2.1.$0^{2,5}$)nonane, n_D^{20} 1.4860, was a colorless liquid miscible with common organic solvents. The mass spectrum confirmed a parent ion peak at 122.

The hydrogenation was repeated using a copper chromite catalyst at 150° C. and 880 p.s.i.g. hydrogen pressure. The hydrogenation was terminated before complete saturation, and a gas-liquid chromatographic analysis of the product mixture indicated the presence of three products, one of which was the above-described tricyclo(4.2.1.$0^{2,5}$)nonane. The two remaining products were separated by a preparative gas-liquid chromatographic technique, and were each shown by mass spectroscopy to have a molecular weight of 120. The two compounds were identified as tricyclo(4.2.1.$0^{2,5}$)non-3-ene and tricyclo(4.2.1.$0^{2,5}$)non-7-ene, formed by hydrogenation of one of the double bonds in the original diene. The retention of the tricyclo(4.2.1.$0^{2,5}$) ring structure was established by conversion of each compound to tricyclo(4.2.1.$0^{2,5}$)nonane upon further hydrogenation.

I claim as my invention:

1. The process for the production of mono- to di-ethylenically unsaturated tricyclo(4.2.1.$0^{2,5}$)nonanes by reacting bicyclo(2.2.1)heptane having from 1 to 2 endo ethylenic linkages connecting non-bridgehead carbon atoms and having as the only non-hydrogen ring substituents from 0 to 6 hydrocarbyl substituents independently having from 1 to 10 carbon atoms, said hydrocarbyls having only aromatic unsaturation, with acetylenic hydrocarbon having a single carbon-carbon triple bond, the only non-hydrogen substituents on which are hydrocarbyl having from 1 to 10 carbon atoms and having only aromatic unsaturation, at a temperature from about 30° C. to about 250° C. and a pressure from about 1 atmosphere to about 100 atmospheres, in the presence of a catalytic amount, said amount being from about 0.01% mole to about 1% mole based on the limiting reactant, of tetrakis(trihydrocarbylphosphite)nickel (0).

2. The process of claim 1 wherein the tetrakis(trihydrocarbylphosphite)nickel (0) is tetrakis[tri(2-ethylhexyl) phosphite]nickel (0).

3. The process for the production of tricyclo(4.2.1.$0^{2,5}$)nona-3,7-dienes by reacting bicyclo(2.2.1)hepta-2,5-diene with acetylenic hydrocarbon having a single carbon-carbon triple bond, the only non-hydrogen substituents on which are hydrocarbyl having from 1 to 6 carbon atoms and having only aromatic unsaturation, at a temperature from about 30° C. to about 250° C. and a pressure from about 1 atmosphere to about 100 atmospheres, in the presence of a catalytic amount, said amount being from about 0.01% mole to about 1% mole based on the limiting reactant, of tetrakis[tri(2-ethylhexyl)phosphite] nickel (0).

4. The process of claim 3 wherein the acetylenic hydrocarbon is 2-butyne.

5. The process for the production of tricyclo(4.2.1.$0^{2,5}$)non-3-enes by reacting bicyclo(2.2.1)hept-2-ene with acetylenic hydrocarbon having a single carbon-carbon triple bond, the only non-hydrogen substituents on which are hydrocarbyl having from 1 to 6 carbon atoms and having only aromatic unsaturation, at a temperature from about 30° C. to about 250° C. and a pressure from about 1 atmosphere to about 100 atmospheres, in the presence of a catalytic amount, said amount being from about 0.01% mole to about 1% mole based on the limiting reactant of tetrakis[tri(2-ethylhexyl)phosphite]nickel (0).

6. The process of claim 5 wherein the acetylenic hydrocarbon is phenylacetylene.

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