This invention relates to a process for producing spirohydrocarbons and particularly for producing a spirohydrocarbon containing a cycloalkadiene ring.

An object of this invention is to produce a spirohydrocarbon having a cyclopentadiene ring. Another object of this invention is to produce 8,8-dimethylspiro[4.5]-decane.

One specific embodiment of this invention relates to a process for producing a spirohydrocarbon which comprises condensing a cycloalkadiene and a dihaloalkane having the structure represented by the formula:

$$
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{X-C-(C)-C-X} & \quad \text{R''-R'''}
\end{align*}
$$

where \( R, R', R'', \text{and} R''' \) are selected from the group consisting of hydrogen and alkyl radicals, \( X \) represents a halogen and \( n \) is an integer from 1 to 5 inclusive and the unsatisfied valences of the group are combined with a member of the group consisting of hydrogen and an alkyl radical.

A further embodiment of this invention relates to a process for producing a spirohydrocarbon which comprises reacting an alpha, omega-dihaloalkane and a sodium addition compound of a cycloalkadiene and an alkali metal.

A further embodiment of this invention relates to a process for producing a spirohydrocarbon which comprises reacting an alpha, omega-dihaloalkane and a sodium addition compound of a cycloalkadiene to form a diolefinc spirohydrocarbon having two quaternary carbon atoms and hydrogcnating said diolefinc spirohydrocarbon to form a saturated spirohydrocarbon having two quaternary carbon atoms.

A still further embodiment of this invention relates to a process for producing a spirohydrocarbon which comprises reacting 1,5-dibromo-3,3-dimethylpentane and disodium cyclopentadiene to form 3,5-(3,3-dimethylpentamethylene)-1,5-cyclopentadiene.

This invention relates to a process for preparing hydrocarbons containing conjugated double bonds and a spiro carbon atom. Such hydrocarbons which are new compositions of matter are formed by the reactions indicated in the following equations:

$$
\begin{align*}
& \text{(1)} \\
& \text{(2)}
\end{align*}
$$

The dihaloalkane in the above equation is 1,5-dibromo-3,3-dimethylpentane. Other suitable dihaloalkanes are those having the structure represented by

$$
\begin{align*}
\text{R} & \quad \text{R'} \\
\text{X-C-(C)} & \quad \text{R''-R'''}
\end{align*}
$$

where \( R, R', R'', \text{and} R''' \) are selected from the group consisting of hydrogen and alkyl radicals, \( n \) is an integer from 1 to 5 inclusive and the unsatisfied valences of the halogen atoms are attached to primary carbon atoms. Poorer yields are obtained when either (or both) halogen atom is attached to a secondary carbon atom and still lower yields are obtained with compounds containing halogen attached to a tertiary carbon atom.

Dihaloalkanes preferred as starting materials in this process are indicated by the following formula:

$$
\begin{align*}
\text{(1)} \\
\text{(2)}
\end{align*}
$$
in which each of \( R^1, R^2, R^3, R^4, R^5 \) and \( R^6 \) represents a member of the group consisting of hydrogen and alkyl radicals, \( X \) represents a halogen, and the characters \( m \) and \( n \) are selected from the members of the group consisting of 0, 1, 2, and 3. The halogens generally preferred are chlorine and bromine. The characters \( m \) and \( n \) are such that their sum has a value of from 0 to 4 and preferably of 1 or 2. When \( m \) and \( n \) are zero Formula 2 is of essentially the same form as Formula 1.

A preferred starting material for this process is thus an alpha, omega-dihaloalkane in which a halogen atom, preferably chlorine or bromine, is combined with each of the two end carbon atoms of an alkane chain containing four or five carbon atoms. Such dihaloalkanes include 1,5-dibromo-3,3-dimethylpentane, 1,4-dibromo-butane, and 1,5-dichloropentane.

Dihaloalkanes containing a quaternary carbon atom such as 1,5-dichloro-3,3-dimethylpentane and the corresponding dibromoalkane may be formed by condensing a monoolefin and a dihaloalkane in which one of the halogen atoms is attached to a tertiary carbon atom, and the other is attached to a primary carbon atom, said condensation being carried out in the presence of a Friedel-Crafts catalyst at a temperature of from about -40° to about 100° C.

Good yields of such dihaloalkanes are obtained by condensing a monoolefin such as ethylene with a dihaloalkane in which the halogens are combined with one tertiary and one non-tertiary carbon atom. Thus ethylene will condense with isopropylidene dichloride (more exactly known as 1,3-dichloro-3-methylbutane) in the presence of aluminum chloride and other Friedel-Crafts catalysts to form 1,4-dichloro-3,3-dimethylpentane.

Cyclopentadiene is a diolefin which has two hydrogen atoms that are readily replaced by sodium or by another alkali metal to form a sodium addition product of said cyclic diolefin which may be reacted with dihaloalkanes of the type described above to form a spirohydrocarbon. Thus reaction of cyclopentadiene sodium with 1,5-dibromo-3,3-dimethylpentane yields 5,5-(3,3-dimethylpentamethylene)-1,3-cyclohexadiene.

Hydrogenation of this unsaturated compound produces 8,8-dimethyl-1,4-decane which may also be referred to as 1,1-tetramethylethylene-4,4-dimethylcyclohexane.

The condensation of a cycloalkadiene with an alpha, omega-dihaloalkane having at least four carbon atoms per molecule may be accomplished in several ways. One method consists in adding the diene to a solution of sodium alkoxide in an alcohol such as ethyl alcohol and then adding the dihaloalkane. The addition of the diene to the solution of sodium alkoxide is preferably carried out at about -20° to 25° C. Reaction with the dihaloalkane may be carried out at temperatures of about -10 to +100° C, preferably at about the reflux temperature of the reaction mixture.

Another procedure consists in adding the diene to a solution of sodium in liquid ammonia and then adding the dihaloalkane. The reaction may be carried out at the reflux temperature of liquid ammonia at atmospheric pressure (ca. 33° C.) but higher temperatures may be used in some cases by employing superatmospheric pressure. Both of these methods have been used to give good yields of the diolefine spirohydrocarbon condensation product.

The following examples are given to illustrate the process of this invention although the data are not introduced with the intention of limiting unduly the broad scope of the invention.

**Example I**

The condensation of cyclopentadiene and 1,5-dibromo-3,3-dimethylpentane was carried out as follows in a glass reactor of 500 cc. capacity. Sodium metal (0.11 mole) was dissolved in 67 cc. of absolute alcohol (redistilled from sodium). The resulting solution was cooled to 2° C. and 7 g. (0.11 mole) of cyclopentadiene was added. A brown precipitate separated, 1,5-dibromo-3,3-dimethylpentane (25 g., 0.10 mole) was added and the stirred mixture was heated to 60° C. While salt precipitated. The temperature was maintained at 60–70° C. for two hours, the product was then cooled, water was added and the product was steam distilled. There was obtained 9 cc. of organic distillate which was taken up in ether and distilled:

<table>
<thead>
<tr>
<th>Cut</th>
<th>B. P. °C.</th>
<th>Press., mm.</th>
<th>Vd., cc.</th>
<th>np²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37–43</td>
<td>2.00</td>
<td>1.5</td>
<td>1.6080</td>
</tr>
<tr>
<td>2</td>
<td>42–45</td>
<td>2.00</td>
<td>1.3</td>
<td>1.6310</td>
</tr>
<tr>
<td>3</td>
<td>46–48</td>
<td>2.00</td>
<td>1.3</td>
<td>1.6760</td>
</tr>
<tr>
<td>Bottoms</td>
<td></td>
<td></td>
<td>1.3</td>
<td></td>
</tr>
</tbody>
</table>

Cut 2 was analyzed. Calcd. for CaH₉: C, 83.83; H, 11.17. Found: C, 86.77; H, 10.86. Reaction of the material (a diene) with air is indicated.

Cut 2 yielded a maleic anhydride adduct.

**Example II**

Cyclopentadiene (18 g., 0.27 mole) was added to a solution of 10 g. (0.42 mole) of sodium in 120 g. of liquid ammonia in a glass-lined reactor equipped with a motor-driven stirrer and surrounded by a suitable cooling bath. 1,5-dibromo-3,3-dimethylpentane (52 g., 0.20 mole) was then added dropwise with stirring during one-half hour. The blue color of the solution disappeared after about two-thirds of the dibromide had been added. The solution was stirred for an additional one hour, water was added, and the organic product was taken up in ether, washed, dried, and distilled:

<table>
<thead>
<tr>
<th>Cut</th>
<th>B. P. °C.</th>
<th>Press., mm.</th>
<th>Vd., cc.</th>
<th>np²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20–29</td>
<td>2.5</td>
<td>1.3</td>
<td>1.6710</td>
</tr>
<tr>
<td>2</td>
<td>29–54</td>
<td>2.5</td>
<td>1.5</td>
<td>1.4700</td>
</tr>
<tr>
<td>3</td>
<td>54–60</td>
<td>2.5</td>
<td>2.0</td>
<td>1.4810</td>
</tr>
<tr>
<td>4</td>
<td>60–66</td>
<td>2.5</td>
<td>1.9</td>
<td>1.4800</td>
</tr>
<tr>
<td>Bottoms</td>
<td></td>
<td></td>
<td>1.9</td>
<td></td>
</tr>
</tbody>
</table>

Cut 4 crystallized when cooled to -78° C. It yielded a maleic anhydride adduct, M. P. 140°. The adduct was analyzed. Calcd. for CaH₆O₄: C, 73.60; H, 7.75. Found: C, 74.51; H, 7.83.

The hydrocarbon formed by the condensation of 1,5-dibromo-3,3-dimethylpentane and cyclopentadiene had the correct boiling point and composition for 5,5-(3,3-dimethylpentamethylene)-1,3-cyclopentadiene and also formed a maleic anhydride adduct having the proper carbon and hydrogen content. This condensation product of an alpha, omega-dihaloalkane and a cycloalkadiene is a member of a new class of hydrocarbons, namely, a conjugate diolefin containing a spiro carbon atom. Also the hydro-
The regeneration of such a conjugated cyclodiolefin containing a spiro carbon atom yields a saturated spirohydrocarbon. Some of the saturated spirohydrocarbons which may be formed by this process also contained two quaternary carbon atoms, that is, a quaternary carbon atom in addition to the spiro carbon atom.

**Example III**

Reaction products obtained in Examples I and II and consisting essentially of dimethylpentamethylene cyclopentadiene were combined and the resulting 10.6 cc. of liquid hydrocarbon was dissolved in 11 cc. of n-pentane and hydrogenated at a temperature of from 50° to 75° C. in the presence of a nickel-diatomaceous earth catalyst. The hydrogenation product was filtered to separate the pentane solution from the catalyst. The pentane solution was then distilled and separated into fractions with the following properties:

<table>
<thead>
<tr>
<th>Cut</th>
<th>B.P., °C</th>
<th>Proc., mm.</th>
<th>B.P. at 760 mm.</th>
<th>Vol., cc</th>
<th>mP°</th>
<th>M.P., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Below 50</td>
<td>2.0</td>
<td>Below 175</td>
<td>41 g</td>
<td>(Pentane)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>42-59</td>
<td>2.0</td>
<td>192-180</td>
<td>0.9</td>
<td>1.408</td>
<td>-29</td>
</tr>
<tr>
<td>2</td>
<td>50-53</td>
<td>2.0</td>
<td>198-181</td>
<td>1.4</td>
<td>1.4710</td>
<td>-28</td>
</tr>
<tr>
<td>3</td>
<td>55-57</td>
<td>2.0</td>
<td>204-308</td>
<td>2.8</td>
<td>1.4698</td>
<td>-28</td>
</tr>
<tr>
<td>4</td>
<td>57-59</td>
<td>2.0</td>
<td>208-309</td>
<td>3.7</td>
<td>1.4698</td>
<td>-28</td>
</tr>
<tr>
<td>Bottoms</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

1 Determined with thermometer in liquid in test tube.  
2 Slightly unsaturated mixture.

Analysis of cut 4. Calcd. for C_{26}H_{54}: C, 86.65; H, 13.35. Found: C, 86.76; H, 13.11. Analysis of cut 3. Found: C, 85.51; H, 12.20. Fraction 4 consisted essentially of 8,8-dimethylsilo[4.5]-decane which may also be referred to as 1,1-tetramethylene-4,4-dimethylcyclohexane.

5. A process for producing a spirohydrocarbon which comprises reacting 1,5-dibromo-3,3-dimethylpentane and disodium cyclopentadiene to form 5,5-(3,3-dimethylpentamethylenel)-1,3-cyclopentadiene.

6. A process for producing a spirohydrocarbon which comprises reacting 1,3-dibromo-3,3-dimethylpentane and disodium cyclopentadiene to form 5,5-(3,3-dimethylpentamethylenel)-1,3-cyclopentadiene, and hydrogenating the latter compound to form 8,8-dimethylsilo[4.5]-decane.

7. 5,5-(3,3-dimethylpentamethylenel) -1,3-cyclopentadiene.

LOUIS SCHEMLING.

**REFERENCES CITED**

The following references are of record in the file of this patent:

**UNITED STATES PATENTS**

- Number: 2,407,214  
  Name: Birch et al.  
  Date: Sept. 10, 1946

**OTHER REFERENCES**

- Thiele: Berichte, vol. 34, 68-71 (1911).