

May 2, 1967

G. WILKE ETAL

3,317,620

CIS,CIS-CYCLODECADIENE-(1,6) AND ITS MANUFACTURE

Filed April 9, 1964

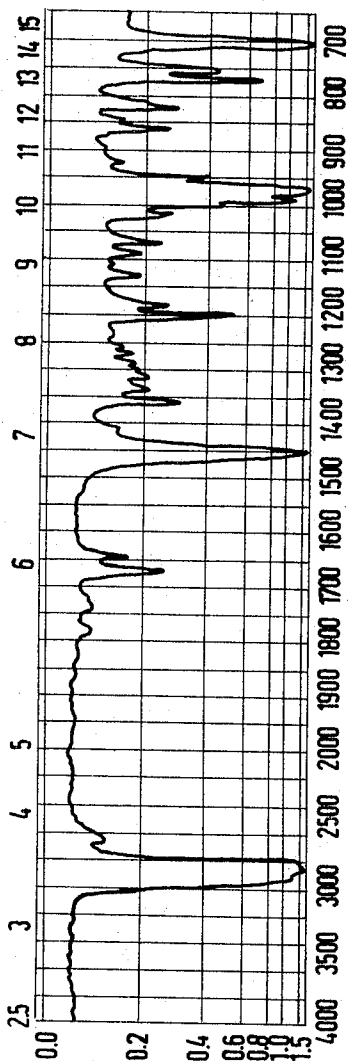


Fig. 1

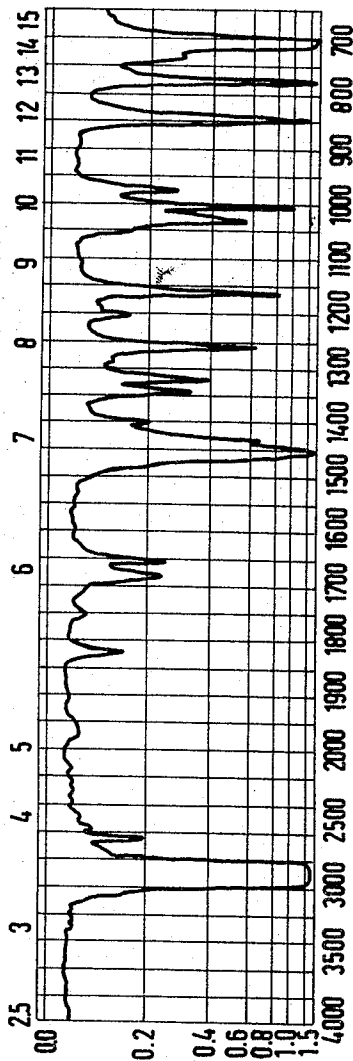


Fig. 2

INVENTORS  
GÜNTHER WILKE, PAUL HEIMBACH  
BY  
*Burgess, Dinklage & Sprung*  
ATTORNEYS

1

3,317,620

## CIS,CIS-CYCLODECA-1,6 AND ITS MANUFACTURE

Günther Wilke and Paul Heimbach, both of Mulheim (Ruhr), Germany, assignors to Studiengesellschaft Kohle m.b.H., Mulheim (Ruhr), Germany, a corporation of Germany

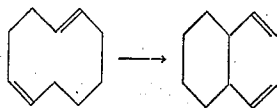
Filed Apr. 9, 1964, Ser. No. 358,457

Claims priority, application Germany, Apr. 10, 1963, St 20,502

15 Claims. (Cl. 260—666)

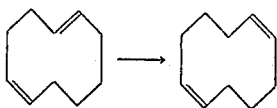
According to pending patent application 267,364 the co-oligomerization of 1,3-diolefins with olefins or acetylenes is feasible and can yield inter alia trans, cis-cyclodecadiene-(1,5), for instance from butadiene and ethylene. This hydrocarbon ring compound is of considerable importance since it can serve as the starting material for the production of  $\alpha,\omega$ -bi-functional derivatives of n-decane.

By further development of the process set forth above it has been found that the cyclodecadiene-(1,5) is thermally a very labile hydrocarbon which is transformed at temperatures between 80 and 150° C. by a Cope rearrangement into 1,2-divinylcyclohexane.



This rearrangement is troublesome in that it can be initiated even in the course of isolating the hydrocarbon by distillation and is only avoided by effecting distillation under greatly reduced pressure. Correspondingly the cyclodecadiene-(1,5) can only undergo further reaction if the reaction temperatures are at the most 100° C.

It has now been discovered that these difficulties can be eliminated if the trans, cis-cyclodecadiene-(1,5) is caused to isomerize to a stable isomer. On the basis of known processes wherein similar hydrocarbon ring structures are isomerized (see, for instance, J. American Chemical Soc. 1961, vol. 83, page 2954) it would be expected, that in the course of a similar isomerization a cyclodecadiene-(1,3) should be formed. Surprisingly it has been found that isomerization proceeds smoothly to the hitherto unknown cis, cis-cyclodecadiene-(1,6) of M.P. 28.5° C.



The constitution of this novel hydrocarbon has been established by hydrogenation, decomposition with ozone and infra red or proton resonance spectra. Of particular importance from the technical standpoint is the fact that the new isomer exhibits a normal thermal stability.

The present invention thus relates to cis, cis-cyclodecadiene-(1,6) and to the manufacture of this hydrocarbon by isomerizing trans, cis-cyclodecadiene-(1,5) in the presence of catalytic quantities of active metals of Group VIII of the Periodic System. Isomerization can conveniently be effected at temperatures of 0–100° C. and as active catalysts there may be named by way of example Raney metals or noble metals separated under hydrogenation conditions, such as palladium which has previously been named or platinum. Generally the metals are obtained in active form by reducing the transition metal compounds with the aid of organo-metallic compounds of elements of Main Groups I to III of the Periodic System or of their hydrides or rather of their complex hydrides or even with these finely divided metals themselves. A further possibility lies in decomposing the labile olefine- or

2

acetylene  $\pi$ -complexes of the transition metals either by heat or through reduction of ligands. In this manner for instance bis-cyclooctadiene-(1,5) nickel yields with hydrogen, cyclo-octane and highly active nickel and bis- $\pi$ -allyl-palladium propane and palladium.

The process of the present invention can be carried out in presence of solvents, as for example, hexane, cyclohexane, benzol, ether or also alcohols when Raney metals are employed as catalysts.

By the present invention the thermally unstable trans, cis-cyclodecadiene-(1,5) obtainable from butadiene and ethylene is converted to a stable isomer. It is recommended that the reaction product of the aforementioned process, containing cyclodecadiene-(1,5) is first caused to undergo isomerization, and thereafter the 10-ring component isolated in the form of the new stable isomer, for example by distillation. The cis, cis-cyclodecadiene-(1,6) is then available for further reactions which call for higher temperatures.

The invention can be illustrated by reference to the following examples:

In each case the procedure followed was on these lines. About 1 gram of a transition metal acetyl acetate is dissolved or suspended in 10 mls. benzene or one of the solvents specified above and reduced with 1 mol equivalent of triethyl aluminum. After the addition of about 10 grams cis, trans-cyclodecadiene-(1,5) the mixture is heated with stirring for 24 hours at 80 to 90° C. After removal of the catalyst the composition of the reaction product can be ascertained by gas chromatography.

The characteristic difference between the I-R spectra of cis,trans-cyclodecadiene-(1,5) and cis,cis-cyclodecadiene-(1,6) is ascertainable at 1165  $\text{cm}^{-1}$ . At this frequency the cis,trans-compound possesses no absorption while the cis,cis-compound shows a strong absorption band. By means of this band, the isomerization in accordance with the invention can be established.

FIG. 1 illustrates the I-R spectra of cis-trans-cyclodecadiene-(1,5), and

FIG. 2 illustrates the I-R spectra of cis, cis-cyclodecadiene-(1,6).

### Example 1

1 gram of nickel (II)-acetylacetonate is reacted with 1 gram of diethyl aluminum ethoxide. The metallic nickel in highly active form thus obtained is employed to isomerize 10 grams cis, trans-cyclodecadiene-(1,5). After working up there is obtained 3.9 grams (39%) divinylcyclohexane and 6.1 grams (61%) cis, cis-cyclodecadiene-(1,6).

### Example 2

1 gram cobalt (III)-acetylacetonate, 1.1 gram diethyl aluminum ethoxide and 10 grams of cis, trans-cyclodecadiene-(1,5) are used for the reaction. After working up there is obtained 1.6 grams (16%) divinylcyclohexane, 1.1 grams (11%) of an unidentified  $\text{C}_{10}$ -hydrocarbon, 6.6 grams (66%) cis,cis-cyclodecadiene-(1,6) and 0.7 grams (7%) of an unidentified  $\text{C}_{10}$ -hydrocarbon.

### Example 3

1 gram iron (III) acetylacetonate, 1.1 gram diethylaluminum ethoxide and 10 grams cis, trans-cyclodecadiene-(1,5) are used for reaction. After working up there is obtained 3.7 grams (37%) divinylcyclohexane, 1.0 grams (10%) of an unidentified  $\text{C}_{10}$ -hydrocarbon, 4.8 grams (48%) cis, cis-cyclodecadiene-(1,6), and 0.5 grams (5%) of an unknown  $\text{C}_{10}$ -hydrocarbon.

### Example 4

0.5 grams palladium (II) acetylacetonate, 0.4 grams diethylaluminum ethoxide and 10 grams cis, trans-cyclo-

decadiene-(1,5) are used for reaction. After working up there is obtained 1.0 grams (10%) divinylcyclohexane and 9.0 grams (90%) of cis, cis-cyclodecadiene-(1,6).

#### Example 5

2 grams Raney nickel are heated with 15 grams cis, trans-cyclodecadiene-(1,5) for two days at 50° C. while stirring. Apart from 5.7 grams of unreacted cis, trans-product there can be isolated 9.3 grams (62%) cis, cis-cyclodecadiene-(1,6).

We claim:

1. Process for the preparation of cis,cis-cyclodecadiene-(1,6) by isomerization of cis,trans-cyclodecadiene-(1,5) which comprises contracting cis,trans-cyclodecadiene (1,5) with a catalytic quantity of a Group VIII metal of the Periodic System in solid particle form.

2. Process according to claim 1, wherein said metal catalyst is obtained by finely dividing a Group VIII metal.

3. Process according to claim 1, wherein said metal catalyst is obtained by reducing a transition metal with the aid of an organo-metallic compound of an element of main Group I and III, its hydride or its complex hydride.

4. Process according to claim 1, wherein said metal catalyst is obtained by decomposing the labile unsaturated  $\pi$  compound of the transition metal by heat or through reduction of ligands.

5. Process according to claim 1, wherein said contacting is effected at a temperature of between 0 and 100° C.

6. Process according to claim 1, wherein said catalyst is a Raney metal.

7. Process according to claim 1, wherein said catalyst is palladium.

8. Process according to claim 1, wherein said catalyst is platinum.

9. Process according to claim 5 which comprises effecting said contacting in the presence of a solvent selected from the group consisting of ethers, aliphatic, cycloaliphatic, and aromatic hydrocarbon liquid in the reaction.

10. Process according to claim 1, wherein said catalyst is Raney metal and said contacting is effected in the presence of an alcohol as solvent.

11. Process according to claim 1, wherein said catalyst is metallic nickel obtained by reduction of nickel-(II)-acetylacetonate.

12. Process according to claim 1, wherein said catalyst is metallic cobalt obtained by reduction of cobalt-(III)-acetylacetonate.

13. Process according to claim 1, wherein said catalyst is metallic iron obtained by reduction of iron-(III)-acetylacetonate.

14. Process according to claim 1, wherein said catalyst is metallic palladium obtained by reduction of palladium-(II)-acetylacetonate.

15. Process according to claim 1, wherein said catalyst is Raney nickel.

#### References Cited by the Examiner

Donald J. Cram et al., J. Am. Chem. Soc., 78, pages 2518-24, 1956.

DELBERT, E. GANTZ, *Primary Examiner*.

V. O'KEEFE, *Assistant Examiner*.

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,317,620

May 2, 1967

Günther Wilke et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 14, for "contracting" read -- contacting --  
same line 14, for "cyclodecadiene" read -- cyclodecadiene- --.

Signed and sealed this 28th day of November 1967.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents