United States Patent Office 3,274,271 Patented Sept. 20, 1966

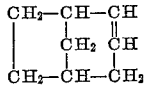
3,274,271

PROCESS FOR THE PREPARATION OF BICYCLO-(3,2,1)-OCTENE-(2)

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No Drawing. Filed Feb. 11, 1963, Ser. No. 257,738
Claims priority, application Germany, Feb. 21, 1962, Sch 31,020
3 Claims. (Cl. 260—666)

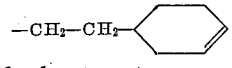
It has been known to prepare bicyclo-(3,2,1)-octene-(2)



by splitting off water from 2-hydroxymethyl-bicyclo-(1,-2,2)-heptane or bicyclo-(3,2,1)-octanol-2 or by rearrangement from bicyclo-(2,2,2)-octene-(2). It has been further known to condense under superatmospheric pressure and at elevated temperature 1,3-cyclohexadiene with ethylene, to form bicyclo-(3,2,1)-octene-2.

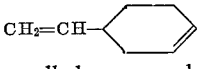
However these processes are either rather costly or have very low yields and hove, therefore, no practical importance.

It has now been found that bicyclo-(3,2,1)-octene-(2) can be advantageously prepared by heating to temperatures above 130° C. aluminum trialkyls, in which at least one alkyl radical is of the formula

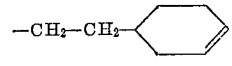


and that it is of advantage to carry out this reaction in the presence of olefins, preferably alpha-olefins. From the reaction mixture the bicyclo-(3,2,1)-octene-(2) is recovered in the manner described hereinafter.

According to a specific modification, instead of the before named aluminum trialkyl compounds a mixture of 4-vinyl-cyclohexene,



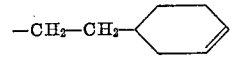
with other aluminum-alkyl compounds is used, which are capable of forming aluminum trialkyl compounds containing at least one alkyl radical of the formula



As examples of being used in the process of this invention 4-vinylcyclohexene or i-butene are named by way of example.

It could not be expected that the Al–C bonds could be added to the double bond of the cyclohexyl ring with the formation of a bicyclic system, that this addition takes place in such uniform manner and that, for example, from a cyclo-hexenyl-ethylaluminum compound bicyclo-(3,2,-1)-octene-(2) can be obtained.

The preparation of the aluminumtrialkyl compounds having at least one alkyl radical of the formula



can be carried out according to methods known by themselves. A favorable procedure is, for example, the reaction of 4-vinylcyclohexene with suitable aluminum-alkyl compounds, particularly aluminum-triisobutyl or aluminum-diisobutylhydride. Furthermore, as 4-vinyl-cyclohexene can be easily obtained by thermal dimerization from butadiene, the process of this invention creates a possibility of obtaining bicyclo-(3,2,1)-octene-(2), with utilization of the petrochemical butadiene which is produced on a large scale.

In carrying out the present invention a commercial scale preferably a continuous cyclic process can be used. For example, a starting amount of aluminum-alkyl compounds is reacted in a suitable reactor with 4-vinylcyclohexene. The bicyclo-(3,2,1)-octene-2 formed is recovered from the reaction product. The aluminum-alkyl compounds and a rest of 4-vinylcyclohexene which eventually has not reacted yet, are likewise separated and returned to the process and mixed there with fresh 4-vinyl-cyclohexene, i.e. conducted in a cycle.

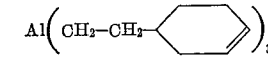
The bicyclo-(3,2,1,)-octene-(2) can be isolated by fractional distillation. It is of advantage in this connection to previously separate the C_8 hydrocarbon by vacuum distillation from the higher molecular, e.g. dimerized, products and aluminum alkyl compounds. From concentrated mixtures the bicyclo-(3,2,1)-octene-(2) can be recovered also by crystallization. After purification by recrystallization and sublimation the product of the invention is a white camphorlike mass which is very volatile and has a melting point, in a sealed tube, of 42.5–43.5° C. and a boiling point of $B.P._{760}=135°$ C. Its index of refraction is $n_D^{50}=1.4689$.

The reactions with aluminum organic compounds must be carried out in conventional manner with the exclusion of oxygen and humidity.

The bicyclo-(3,2,1)-octene-(2) is of particular utility and importance in the preparation of intermediate products which are capable of polymerization and polycondensation.

Example 1

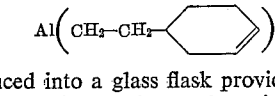
412 g. of 4-vinylcyclohexene are heated to 180° C. together with 226 g.



for 2 hours in a one liter shaking autoclave. The pressure did not exceed 5 atmospheres superatmospheric pressure. After permitting the autoclave to cool, the reaction mixture was transferred to a distillation device provided with a Claisen attachment. Upon stirring and heating up to 110° C. under a pressure of 4 torr, 210 g. of distillate were collected in the well-cooled receiver. The distillate contained 80% of bicyclo-(3,2,1)-octene-(2). The pure bicyclo-(3,2,1)-octene-(2) was recovered by fractional distillation with an efficient column.

Example 2

300 g. of 4-vinylcyclohexene and 303 g. of



were introduced into a glass flask provided with a reflux cooler and a stirring device. The mixture was heated under reflux until the temperature reached 150° C. The

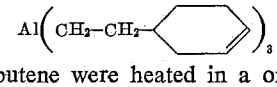
mixture was then kept under stirring for 5 additional hours at 150° C., then permitted to cool and the reaction mixture was then processed in the manner described in the above Example 1. 130 g. of distillate containing 31% of bicyclo-(3,2,1)-octene-(2) were obtained, from which the pure product was recovered in the manner described in the above Example 1.

Example 3

2511 g. of 4-vinylcyclohexene and 544 g. $Al(i\text{-}C_4H_9)_2H$ were heated in a 5 liter shaking autoclave for 3 hours to 180° C. The pressure reached thereby about 20 atmospheres of super-atmospheric pressure. The autoclave was permitted to cool and the reaction mixture was transferred to a distillation apparatus provided with a Claisen attachment. Upon stirring and heating to 110° C., under a pressure of 10 torr, 998 g. distillate were collected in the well cooled receiver. Subsequently, the distillate was subjected to distillation with a short fractionating attachment under atmospheric pressure. Between 130° and 140° C. head temperature 924 g. of distillate were obtained, which contained 87% of bicyclo-(3,2,1)-octene-(2) and from which the pure product was isolated in the manner described in the above Example 1.

Example 4

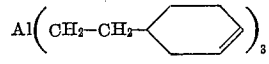
243 g. of



and 250 g. i-butene were heated in a one liter shaking autoclave for 2 hours to 180° C. After cooling, the excess i-butene was discharged and the reaction mixture was transferred into a distillation apparatus provided with a short fractionating attachment. The residual i-butene was removed under vacuum at about 30 torr. Subsequently, under stirring heating was carried out up to 110° C. under 5–7 torr. Thereby, 96 g. of distillate passed to the cooled receiver. To the distillate which contained some aluminum alkyl, carefully some dilute hydrochloric acid was added; it was then shaken, washed with water and dried over potassium carbonate. 89 g. of a mixture of hydrocarbons containing 46% bicyclo-(3,2,1)-octen-(2) were obtained.

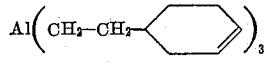
Example 5

97 g. of



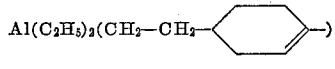
are heated in a round-bottomed flask provided with a reflux cooler for 5 hours to 150–180° C. After cooling down of the reaction mass, the yellow, very viscous reaction product is caused to pass at 130–140° C. and 0.1–2 torr through a thin-layer evaporator. Thereby 8 g. of material distilled over and were recovered in a trap cooled with dry CO_2 and acetone. It has been found by means of a gas chromatogram that the distillate consisted to about 80% of bicyclo-(3,2,1)-octene-2.

The preparation of the compound



from aluminum triisobutyl and 4-vinylcyclohexene is described in Metallorganische Verbindungen, XL, "Synthesis of Alcohols from Organo-Aluminum Compounds," K. Ziegler, F. Krupp and K. Zosel, Liebig's Annalen der Chemie, 629, 241 (1960).

The preparation of the compound



from aluminum diethyl hydrid and 4-vinylcyclohexene is described in Metallorganische Verbindungen, XIX, "Reaction of the Aluminum-Hydrogen Bond with Olefins,"

K. Ziegler, H. G. Gellert, H. Martin, K. Nagel and J. Schneider, Liebig's Annalen der Chemie, 589.

From the α-olefins primarily 4-vinylcyclohexene and i-butene are used. Bicyclo-(3,2,1)-octene-2 is formed also in the presence of mixtures of α-olefins, such as propene and 4-vinyl-cyclohexene and also butene-1 and 4-vinylcyclohexene.

Purification of the bicyclo-(3,2,1)-2-octene was carried out from highly concentrated, but still liquid (or remelted) crude product.

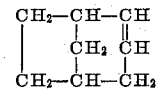
It has been known that bicyclo-(3,2,1)-octene-2 can be converted over bicyclooctanol, and over the bicyclooctanon into the cyclopentane-(1)-carboxylic acid-3-acetic acid. This dicarboxylic acid can be condensed with dioles or diamines to polyesters or polyamides which can be used as thermoplastic materials.

The temperature of the reaction is carried out in the range of 130–350° C. and under a pressure in the range between 1 atmosphere up to the pressure which corresponds to the vapor tension of the reaction mixture at the reaction temperature used.

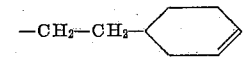
The lower limit for the proportions of olefin and aluminum compound is at 1:0.1. In the example 5, the upper limit is stated with an aluminum compound without olefin-reactant.

What is claimed is:

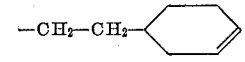
1. A process for the preparation of bicyclo-(3,2,1)-octene-(2)



comprising heating aluminum trialkyl compounds, in which at least one alkyl radical is

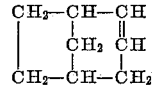


and the rest of the alkyl radicals is selected from the group consisting of

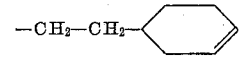


and lower alkyl radicals, to a temperature in the range of 130° C. to 350° C. and separating the bicyclo-(3,2,1)-octene-(2) from the reaction mixture, the aluminum trialkyl compound being heated together with i-butene.

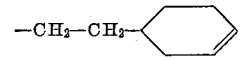
2. A process for the preparation of bicyclo-(3,2,1)-octene-(2)



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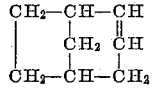


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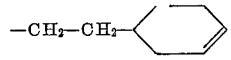


and lower alkyl radicals, to a temperature in the range of 130° C. to 350° C. and separating the bicyclo-(3,2,1)-octene-(2) from the reaction mixture, the aluminum trialkyl compound being heated together with an alpha-olefin.

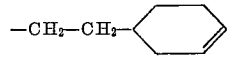
3. A process for the preparation of bicyclo-(3,2,1)-octene-(2)



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and the rest of the alkyl radicals is selected from the group consisting of



and lower alkyl radicals, to a temperature in the range of 130° C. to 350° C. and separating the bicyclo-(3,2,1)-octene-(2) from the reaction mixture, the aluminum trialkyl compound being heated together with 4-vinylcyclohexene.

References Cited by the Examiner

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2,826,598 3/1958 Ziegler et al. ---------- 260—666

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