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DIMERIZATION PROCESS

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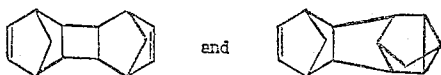
5 Claims. (Cl. 260-666)

ABSTRACT OF THE DISCLOSURE

Bicycloheptadiene dimer mixtures, useful as high energy fuels, are prepared by intimately contacting bicyclo(2.2.1)hepta-2,5-diene at substantially atmospheric pressure and at a temperature above 140° C. in the presence of a zero-valent iron complex as catalyst.

This invention relates to an improved process of dimerizing bicyclo(2.2.1)hepta-2,5-diene.

Methods are available in the art for effecting the dimerization of bicyclo(2.2.1)hepta-2,5-diene in the presence of metal catalysts wherein the metal is present in a reduced oxidation state. For example, the Belgian Patent No. 626,407 issued June 21, 1963, to Shell Internationale Research Maatschappij N.V., discloses a dimerization process employing as catalyst, inter alia, a zero-valent complex of iron, nickel or cobalt. Broadly speaking, the disclosed process results in the production of a mixture of bicycloheptadiene dimers represented by the formulas



which are further identified by the systematic chemical names pentacyclo(8.2.1.1^{4,7}.0^{2,9}.0^{3,6})tetradeca-5,11-diene and hexacyclo(7.2.1.1^{3,7}.1^{5,13}.0^{2,8}.0^{4,6})tetradec-10-ene respectively. The dimer mixtures are useful as high energy fuels, in part because of a low solidification point and a relatively high heat of combustion per unit volume. Dimer mixtures having the more desirable properties, particularly the lower solidification points, are those having a high proportion of the hexacyclotetradecene isomer and in order to prepare such mixtures a relatively high dimerization temperature is required. According to the process of the Belgian patent, superatmospheric pressure is required to maintain the bicycloheptadiene reactant in the liquid phase during a dimerization process when the reaction temperature employed is higher than the normal boiling point of the bicycloheptadiene, i.e., higher than 89.2° C. Thus, the process of the Belgian patent requires the use of pressure equipment and batchwise operation in order to produce the more desirable dimer mixtures.

It is an object of the present invention to provide an improved method of dimerizing bicycloheptadiene. More particularly, it is an object to provide a dimerization process employing a high reaction temperature but a relatively low pressure. An additional object is to provide a process adaptable for a continuous type operation.

It has now been found that these objects are accomplished by the process of initially intimately contacting bicycloheptadiene and a zero-valent iron catalyst at a temperature above the normal boiling point of the bicycloheptadiene and at substantially atmospheric pressure. The process of the present invention is characterized by the formation of dimer mixtures having the desirable properties associated with high temperature

dimerization and yet is adaptable for continuous operation at or about atmospheric pressure. Although it is not desired to be bound by any particular theory, it appears probable that the activity of the iron catalyst under the reaction conditions employed is such that the rate of bicycloheptadiene dimerization is more rapid than the rate of vaporization. As a consequence, the dimerization process is operable at substantially atmospheric pressure at a temperature above the normal boiling point of the bicycloheptadiene reactant without undue vapor-phase loss of the monomeric reactant.

The catalyst employed comprises iron in a zero oxidation state stabilized by complex formation with one or more stabilizing ligands. Although the precise catalytic species is not known with certainty it is considered probable that in the presence of the large excess of bicycloheptadiene and/or bicycloheptadiene dimer of the reaction mixture, the iron is complexed with bicycloheptadiene monomer and/or dimer.

In one modification, a complex of iron with bicycloheptadiene is preformed and is added to the reaction mixture as such. Methods of forming complexes of this type are known and broadly comprise reacting a hydrocarbon-soluble iron compound with a suitable reducing agent in the presence of the bicycloheptadiene ligand. Illustrative of suitable hydrocarbon-soluble iron compounds are the acetylacetonate, the acetoacetic acid ester enolates, the dialkylsalicylates and the alcoholates. Preferred as the reducing agent is a compound of aluminum, e.g., a trialkylaluminum or a dialkylaluminum alkoxide wherein the alkyl moieties are alkyl of up to 4 carbon atoms. The preparation of the iron complex is typically conducted in an inert solvent, e.g., aromatic hydrocarbons or ethers, and the resulting product mixture is suitable for use as catalyst in the process of the invention, although preferably some or all excess solvent is removed to afford a higher catalyst concentration.

In an alternate and generally preferred modification, the zero-valent iron catalyst is prepared in situ as by mixing the bicycloheptadiene, a hydrocarbon-soluble iron compound and the reducing agent at the time of introduction of the resulting mixture into the reaction zone wherein dimerization is to occur. A particularly facile method of in situ catalyst formation comprises dissolving the iron compound in a portion of the bicycloheptadiene reactant and dissolving the aluminum-containing reducing agent in the remaining portion. Intimate contact of the two solutions in the heated reaction zone results in formation of the active catalyst and subsequent substantially immediate dimerization.

Regardless of the method of its production, the iron catalyst is employed in catalytic quantities. In general, amounts of catalyst from about 0.0001 gram-atom to about 0.01 gram-atom of iron per mole of bicycloheptadiene are satisfactory, with amounts of iron from about 0.0006 gram-atom to about 0.001 gram-atom of iron per mole of bicycloheptadiene being preferred.

Dimerization of the bicycloheptadiene is effected by initially intimately contacting the reactant and catalyst at a temperature of at least about 140° C. It should be appreciated that the dimerization process is conducted at substantially atmospheric pressure and at a temperature considerably higher than the normal boiling point of the bicycloheptadiene monomer although lower than the boiling point of the dimer product. It is therefore apparent that the reaction temperature must allow the dimerization to proceed at a rate more rapid than the rate of monomer vaporization. When the reactant and catalyst are contacted at a temperature above the normal boiling point of the reactant but below about 140° C., the reaction rate is not sufficiently great and substan-

tial loss of reactant through vaporization is observed. There does not appear to be a critical upper temperature limitation, but temperatures above about 200° C. offer no further advantage. Particularly preferred are temperatures from about 170° C. to about 190° C.

One advantage of the process resides in the use therein of pressures that are substantially atmospheric, thereby obviating the requirement for special pressure equipment. Pressures from about 0.5 atmosphere to about 5 atmospheres are suitable, although in most instances no effort is made to control the pressure and ambient pressure is employed.

The method of contacting reactant and catalyst is of importance to the successful operation of the process. As previously stated, contact of reactant and catalyst at a temperature below about 140° C. results in vapor-phase loss of reactant and/or premature dimerization to comparatively undesirable dimer product mixtures. It is therefore desired that the reactant and catalyst be initially contacted at reaction temperature. The physical method of intimately contacting catalyst and reactant is not critical and conventional methods of providing such intimate contact are satisfactory. Best results are obtained when some provision is made in the reaction zone for promoting more rapid heat transfer, as by placing in the reaction zone an inert material which is maintained at the desired reaction temperature. Particulate solids or liquid diluents which are inert to the reactant, catalyst and products are in general satisfactory although a preferred modification comprises charging to the reactor a small quantity of previously prepared bicycloheptadiene dimer to serve as a heat transfer agent, thereby avoiding the necessity for additional product purification or separation operations.

The process is adaptable for operation in a batchwise manner as by contacting the reactant and catalyst in a conventional bulk reactor. Alternatively, however, the process is suitably conducted in a continuous manner as by continuously removing dimer product from the reaction zone as additional monomer and catalyst are introduced. By any modification, the dimer product is separated from unreacted starting material, reaction byproducts and catalyst by conventional methods such as fractional distillation, fractional crystallization, selective extraction or the like. The recovered starting material is suitably recycled as are the catalyst residues, obtained for example by vapor phase removal of unreacted starting material and at least a substantial, preferably a major, proportion of the dimer product, which may be employed to catalyze additional dimerization.

The bicycloheptadiene dimer product, as previously stated, is useful as a high energy fuel, particularly as a fuel for jet aircraft and like applications where a volume savings is of advantage. The dimer product mixtures of the process are characterized by the presence of a major proportion, e.g., 60–70%, of the above-depicted hexacyclotetradecene and exhibit a high heat of combustion per unit volume and a low solidification point, e.g., below –40° C. The dimer product is useful as a fuel per se or is mixed with conventional fuels such as gasoline, kerosene and the like.

To further illustrate the improved process of the invention, the following examples are provided. It should be understood that the details thereof are not to be regarded as limitations, as they may be varied as will be understood by one skilled in this art.

Example I

To a reactor equipped with stirring means was charged 5 g. of bicycloheptadiene dimer and the reactor was heated to 150° C. To the reactor was simultaneously added in a dropwise manner over a 1 hour period two solutions, one of which consisted of 0.295 g. of iron (III) acetylacetonate dissolved in 60 g. of bicycloheptadiene and the other of which consisted of 0.525 g. of triethylaluminum dissolved in 60 g. of bicycloheptadiene. An exothermic

reaction began immediately upon mixing and the reactor temperature varied from 155° C. to 162° C. At the conclusion of the dropwise addition, the flask was cooled and the products were separated by fractional distillation. The conversion of bicycloheptadiene was 86% and the yield of bicycloheptadiene dimer based on bicycloheptadiene converted was 94%. The percentage of the hexacyclotetradecene isomer, as determined by gas-liquid chromatography, was 68.4% and the solidification point of the mixture was –70° C.

Example II

The procedure of Example I was repeated except that the rate of addition was increased by a factor of three. The reaction temperature fluctuated between 175° C. and 195° C. Under these conditions the conversion of bicycloheptadiene was 79% and the selectivity to bicycloheptadiene dimer was 91%. The percentage of the hexacyclotetradecene isomer was 72.2% and the solidification point of the mixture was below –70° C.

Example III

The procedure of Example I was repeated employing an equivalent amount of nickel acetylacetonate and also cobalt acetylacetonate in place of the iron acetylacetonate of that example. In each case, no dimerization was obtained.

Example IV

To a reactor of 600 ml. capacity was charged a small quantity of bicycloheptadiene dimer and the reactor was heated to 150° C. Equal volumes of a 0.5% wt. solution of iron acetylacetonate in bicycloheptadiene and a 0.95% wt. solution of triethylaluminum in bicycloheptadiene were simultaneously introduced continuously into the reactor and the product mixture was continuously removed by suction at a constant liquid level. At a bicycloheptadiene liquid throughput of 2.0–2.4 liters per hour, corresponding to an average residence time of approximately 5 minutes, the reaction temperature varied between 175° C. and 183° C. The product mixture was fractionally distilled to recover dimer product and unconverted bicycloheptadiene. The conversion of bicycloheptadiene was 86% and the selectivity to dimer was 95.5%.

When this continuous process was repeated employing a throughput of 5.8 liters of bicycloheptadiene per hour, the reaction temperature was 160–170° C. The conversion of bicycloheptadiene was 87% and the selectivity to dimer was 93%.

Example V

The procedure of Example IV was repeated employing a catalyst concentration of one-half that of Example IV, i.e., the concentration of iron acetylacetonate was 0.25% wt. and the concentration of triethylaluminum was 0.475% wt. At a throughput of 1 liter per hour, the reaction temperature varied from 155° C. to 160° C. The bicycloheptadiene conversion was 80% and the selectivity to dimer was 97%.

I claim as my invention:

1. In the process of producing bicyclo(2.2.1)hepta-2,5-diene dimer mixture consisting essentially of pentacyclo(8.2.1.1^{4,7}.0^{2,9}.0^{3,8})tetradeca-5,11-diene and hexacyclo(7.2.1.1^{3,7}.1^{5,13}.0^{2,8}.0^{4,6})tetradec-10-ene by intimately contacting the bicycloheptadiene and a zero-valent iron complex as catalyst, the improvement which consists essentially of producing a dimer mixture wherein said hexacyclotetradecene dimer is the major dimer product by feeding the bicycloheptadiene as liquid into a reaction zone maintained at a temperature of from about 140° C. to about 200° C. and at substantially atmospheric pressure and immediately intimately contacting the bicycloheptadiene in the reaction zone with said iron catalyst having ligands selected from bicycloheptadiene and bicycloheptadiene dimer and controlling the feed rate of

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bicycloheptadiene to the reaction zone to obtain substantially complete dimerization and a minimum loss of bicycloheptadiene as vapor.

2. The process of claim 1 wherein the temperature is from about 170° C. to about 190° C.

3. The process of claim 1 wherein the catalyst is formed in situ by reaction of a hydrocarbon soluble iron compound selected from iron acetylacetonate, iron acetoacetic acid ester enolates, iron dialkylsalicylates and iron alcoholates and supplied to the reaction zone dissolved in a portion of the bicycloheptadiene and an aluminum compound selected from trialkylaluminum and dialkylaluminum alkoxide and supplied separately to the reaction zone dissolved in another portion of the bicycloheptadiene.

4. The process of claim 3 wherein the catalyst is formed in situ by reaction of iron (III) acetylacetonate and triethylaluminum.

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5. The process of claim 1 wherein, subsequent to said intimate contacting, the unreacted bicycloheptadiene and at least a major proportion of said bicycloheptadiene dimer are removed from the resulting product mixture as a vapor phase, and the resulting residue containing catalyst is contacted with additional bicycloheptadiene in the reaction zone.

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