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3,282,663
BICYCLOHEPTADIENE OLIGOMERS

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7 Claims. (Cl. 44-80)

This application is a continuation-in-part of co-pending application U.S. Serial No. 257,090, filed February 8, 1963, now abandoned.

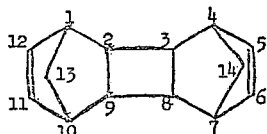
This invention relates to mixtures of dimers and trimers of bicycloheptadiene.

Dimers of bicyclo(2.2.1)hepta-2,5-diene, herein referred to as bicycloheptadiene, are known in the art. For example, the production in low yield of bicycloheptadiene dimers in the presence of iron, nickel or cobalt carbonyl is disclosed by Bird et al. in *Tetrahedron Letters*, 11, 373 (1961) and in *Chemistry and Industry*, 20 (1960).

It is an object of the present invention to provide novel compositions comprising mixtures of bicycloheptadiene dimers, which compositions are characterized by relatively low melting points and by comparatively high heats of combustion per unit volume.

It has now been found that these objects are accomplished by providing bicycloheptadiene dimer and trimer mixtures of controlled composition, that is, mixtures comprising regulated proportions of particular bicycloheptadiene dimers. The dimer and trimer mixture compositions of the present invention have relatively low melting points and relatively high heats of combustion per unit volume, and thus are well suited for use as high energy fuels and propellants which require this unique combination of the above properties.

The compositions of the present invention comprise mixtures of bicycloheptadiene dimers with a minor, if any, proportion of bicycloheptadiene trimer. The dimer compositions are herein considered to consist substantially of bicycloheptadiene dimers, however, it should be understood that the presence of minor proportions of bicycloheptadiene trimer, e.g., less than about 5%, is not excluded, although the trimer is not invariably observed in the oligomer compositions of the invention. The bicycloheptadiene dimer mixtures of the present invention consist essentially of dimers having one of two general formulas. One type of component of typical bicycloheptadiene dimer mixtures comprises compound(s) represented by the systematic chemical name of pentacyclo(8.2.1.0^{2,9}.0^{3,8}.1^{4,7})tetradeca-5,11-diene. Such materials are represented by the structural formula



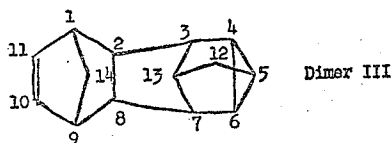
Dimer I
Dimer II

wherein the added numerals indicate one conventional method of identifying the relative locations of the carbon atoms present. It should be appreciated that the above-depicted pentacyclic structure is of necessity in two dimensions and that there exists the possibility of stereoisomers of the above pentacyclic formula, varying, for example in cis-trans and/or exo-endo relationships. Although the precise stereochemical relationships are not known with certainty, two stereoisomers of this formula are customarily observed in the dimer mixtures of the invention. One of these stereoisomers of the above pentacyclo-tetradecadiene is characterized by a melting point of 67-68° C., and this isomer is herein for convenience

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termed Dimer I. The second observed stereoisomer of this formula is characterized by a melting point of 89° C. and this isomer is herein for convenience termed Dimer II. These stereoisomeric dimer forms are more fully identified in Table I below.

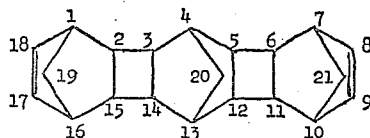
The second type of bicycloheptadiene dimer observed in the dimer mixtures of the invention is represented by the systematic chemical name of hexacyclo(7.2.1.0^{2,8}.1^{3,7}.1^{5,13}.0^{4,6})-tetradec-10-ene and is depicted by the structural formula



Dimer III

wherein the added numerals indicate one conventional method of identifying the relative locations of the carbon atoms present. Although it is apparent that the possibility of stereoisomerism also exists in the hexacyclic structure, the presence of stereoisomers of this structure is not readily detected, there apparently being only one readily identified compound present of this structure. This hexacyclo-tetradecene dimer, characterized by a melting point of -20° C., is herein for convenience termed Dimer III, and is more fully identified in Table I below.

As previously stated, the presence, on occasion, of a bicycloheptadiene trimer is also observed. This trimer is considered to be represented by the formula



wherein the added numerals identify the relative locations of the carbon atoms present. The trimer has the systematic chemical name of octacyclo-(14.2.1.0^{2,15}.0^{3,14}.1^{4,13}.0^{5,12}.0^{6,11}.0^{7,10}) heneicos-8,17-diene and is characterized by a melting point of 201° C. This trimer is described more fully in Table I below.

The method of producing the bicycloheptadiene dimer mixtures is not critical, except in so far as the method of production influences the relative proportions of the various dimers in the resulting mixture. The preferred method of production comprises maintaining bicycloheptadiene at a temperature above about 90° C. and at a pressure sufficiently elevated to maintain the reaction mixture in the liquid phase, in the presence of catalytic quantities of a low-valent Group VIII metal complex catalyst, particularly a zero-valent-metal complex wherein the metal is iron or cobalt. Metal complexes of a variety of types are suitably employed but best results are obtained through utilization of metal-olefin complexes, particularly metal-bicycloheptadiene complexes. Such complexes are employed as preformed materials or are prepared in situ, from other complexes, e.g., a phosphine complex, or by reaction of a metal derivative, e.g., the acetylacetonate, the diacetyl dioximes, the bis(acrylonitrile) derivative or the like, with a reducing agent such as a trialkyl aluminum, e.g., triethyl aluminum, in the presence of bicycloheptadiene. It is not generally necessary to employ a solvent in the dimerization process, as the metal complex catalysts customarily are soluble in the bicycloheptadiene reactant, but on occasion the use of a solvent may be desirable and inert solvents including aromatic hydrocarbons, e.g., benzene or toluene, or others such as tetrahydrofuran are suitably employed.

The bicycloheptadiene dimers prepared in this manner are isolated and/or separated by conventional means, as

by fractional distillation, selective extraction, chromatographic techniques or the like. Alternatively a dimer mixture is recoverable by distillation subsequent to removal of any unreacted bicycloheptadiene and is suitably utilized without further purification or separation.

The bicycloheptadiene dimer compositions of the present invention find utility as high energy fuels, particularly as fuels for jet aircraft, because the high heat of combustion per unit volume of the dimer compositions renders the compositions eminently suitable for applications wherein a volume saving is desired. A consideration relating to dimer proportions, however, is based on the desirability of employing a fuel having a comparatively low melting point in such applications where low temperatures are likely encountered. The dimer mixtures of the invention most advantageously employed as high energy fuels are those characterized by a melting point no higher than -15°C ., preferably no higher than -30°C ., or even lower, e.g., no higher than -100°C .

It is apparent from consideration of the melting points of the individual dimers as above described that the melting point of any given dimer mixture will be greatly dependent upon the relative proportion of the dimer isomers therein. For example, it may be broadly stated that the melting point of a dimer mixture will increase with an increasing proportion of Dimer I, but will decrease with increasing proportions of Dimer III. The following data illustrate the effect on dimer mixture melting point when the composition thereof is varied.

Mixture	Dimer I, Percent wt.	Dimer II, Percent wt.	Dimer III, Percent wt.	Melting Point, $^{\circ}\text{C}$.
A.....	29.2	22.4	48.4	-15
B.....	13.5	27.2	59.2	-35
C.....	6.2	26.8	67.0	-75

To obtain the properties desired of the bicycloheptadiene dimer compositions of the invention, it is preferred that the percentage by weight of Dimer III therein be at least 40%, and preferably at least 55%. Compositions having the most desirable melting points are those wherein the weight percentage of Dimer III is at least 40%, and the weight percentage therein of Dimer I is less than 30% and preferably less than 20%.

The bicycloheptadiene dimer mixtures provided by the present invention are useful as high energy fuels, as previously stated, but are additionally useful in other applications. For example, the dimers are chlorinated to form insecticidal materials or are epoxidized to the corresponding epoxy derivatives which are suitably utilized as precursors of epoxy resins.

To further illustrate the novel compositions 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 80 ml. of benzene was added 90 g. of bicycloheptadiene and 2 g. of tetrakis(triphenylphosphine) nickel and the resulting mixture was heated for 3 hours at 80°C . The resultant product mixture was separated from the catalyst by steam distillation and the organic phase was fractionally distilled. There was obtained 10 g. of unconverted bicycloheptadiene and 50 g. of colorless liquid having a boiling point of 50°C . at 0.001 mm., which liquid was shown by infrared spectrum, elemental analysis, molar refraction, molecular weight and chemical behavior to be a mixture of bicycloheptadiene dimers. The gas-liquid chromatogram of this liquid showed the presence of the three isomers herein designated Dimer I, Dimer II and Dimer III. The dimers were separated by

preparative gas-liquid chromatographic techniques and the physical properties of the isomers as shown in Table I below were determined.

The distillation residue obtained above consisted of 4 g. of a crystallized compound with a melting point of 201°C ., which on the basis of infrared spectrum, elemental analysis, molecular weight and chemical behavior was assigned the trimer structure above depicted. The bicycloheptadiene conversion was 89%; the dimer yield was 63% and the trimer yield was 5%.

TABLE I

Properties	Dimer I	Dimer II	Dimer III	Trimer
Molar Refraction:				
Calc.....	54.93		53.17	
Found.....	54.6		53.24	
Molec. Wt.:				
Calc.....	184.3	184.3	184.3	276
Found.....	192	188	190	290
Analysis:				
C, Percent wt.—				
Calc.....	91.25	91.25	91.25	91.25
Found.....	91.10	91.09	91.01	91.30
H, Percent wt.—				
Calc.....	8.75	8.75	8.75	8.75
Found.....	8.82	8.79	8.69	8.87
Melting Point, $^{\circ}\text{C}$	67-68	85-89	-20	201
Boiling Point, $^{\circ}\text{C}/\text{mm. Hg}$		(decomp.) 75/0.2	76/0.2	
Refractive Index, n_D^{20}		1.5427	1.5476	
Heat of Combustion, cal./cm. ³	12,330	11,052	11,330	
Hydrogen Uptake, moles/mole.....	2	2	1	2

Example II

A series of bicycloheptadiene dimerizations was conducted by charging to an autoclave a filtered mixture of approximately 60% of the bicycloheptadiene to be employed and a quantity of iron acetylacetonate calculated to provide a final solution 1% by weight iron-bicycloheptadiene complex. The reactor was evacuated, heated in a water bath to 80°C ., and triethyl aluminum dissolved in the remaining bicycloheptadiene was introduced at a pressure of 1.5 atmospheres. The pressure in the autoclave rose for a few seconds to about 3 atmospheres and then rapidly fell to zero. The autoclave was maintained at temperatures from about 100°C . to about 150°C . in an oil bath for a time of from about 0.25 hour to about 1 hour. Upon cooling, the product was fractionally distilled at reduced pressure. In each case, the dimer product mixture contained a relatively high percentage of Dimer III, and had a melting point below -30°C ., and frequently the dimer product mixture had a melting point below -100°C .

We claim as our invention:

1. A composition useful as a high energy fuel comprising a low-melting mixture of bicycloheptadiene dimers, said mixture having at least 40% by weight of hexacyclo(7.2.1.0^{2,8}.1^{3,7}.1^{5,13}.0^{4,6})tetradec-10-ene.
2. A composition useful as a high energy fuel comprising a low-melting mixture of bicycloheptadiene dimers, said mixture having at least 40% by weight of hexacyclo(7.2.1.0^{2,8}.1^{3,7}.1^{5,13}.0^{4,6})tetradec-10-ene and having a melting point no higher than -15°C .
3. A composition useful as a high energy fuel comprising a low-melting mixture of bicycloheptadiene dimers, said mixture having at least 40% by weight of hexacyclo(7.2.1.0^{2,8}.1^{3,7}.1^{5,13}.0^{4,6})tetradec-10-ene and less than 30% by weight of the pentacyclo(8.2.1.0^{2,9}.0^{3,8}.1^{4,7})tetradeca-5,11-diene isomer having a melting point of $67-68^{\circ}\text{C}$.
4. The composition of claim 3 having a melting point no higher than -30°C .
5. A composition useful as a high energy fuel comprising a low-melting mixture of bicycloheptadiene dimers, said mixture having at least 40% by weight of hexacyclo(7.2.1.0^{2,8}.1^{3,7}.1^{5,13}.0^{4,6})tetradec-10-ene and less than 20% by weight of the pentacyclo(7.2.1.0^{2,9}.0^{3,8}.1^{4,7})tetradeca-5,11-diene isomer having a melting point of $67-68^{\circ}\text{C}$.

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6. The composition of claim 5 having a melting point no higher than -100° C.

7. A composition useful as a high energy fuel comprising a low-melting mixture of bicycloheptadiene dimers, said mixture having at least 55% by weight of hexacyclo-⁵ (7.2.1.0^{2,8}.1^{3,7}.1^{5,13}.0^{4,6})tetradec-10-ene and less than about 20% by weight of the pentacyclo(8.2.1.0^{2,9}.0^{3,8}.1^{4,7})tetradeca-5,11-diene isomer having a melting point of $67-68^{\circ}$ C., said mixture having a melting point no higher than -30° C.

References Cited by the Examiner

UNITED STATES PATENTS

3,002,829 10/1961 Kolfenbach et al. ----- 44-80 15

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FOREIGN PATENTS

1,136,329 9/1962 Germany.
831,350 3/1960 Great Britain.

OTHER REFERENCES

Bird et al.: "Dimerization of Bicycloheptadiene by Metal Carbonyls," Tetrahedron Letters, No. 11, p. 373, 1961.

Bird et al.: "Reaction of Bicycloheptadiene With Metal Carbonyls," Chemistry and Industry, pp. 20-21, Jan. 2, 1960.

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