United States Patent Office 3,712,922 Patented Jan. 23, 1973

3,712,922

UNSATURATED QUATERNARY ALKYLATED FATTY ACIDS AND DERIVATIVES

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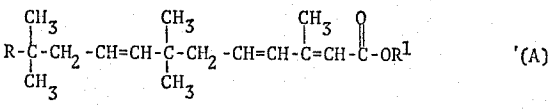
No Drawing. Filed Sept. 28, 1970, Ser. No. 76,280
Int. Cl. C07c 69/52; A01n 9/24
U.S. Cl. 260—410.9 R 13 Claims

ABSTRACT OF THE DISCLOSURE

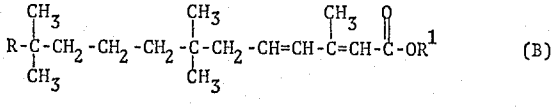
Aliphatic quaternary alkyl compounds having unsaturation at C-2,3, C-4,5 and/or C-8,9 and intermediates therefor useful as insect control agents, lubricants, plasticizers and odorants.

This invention relates to novel unsaturated quaternary alkyl compounds, intermediates therefor, syntheses thereof and the control of insects.

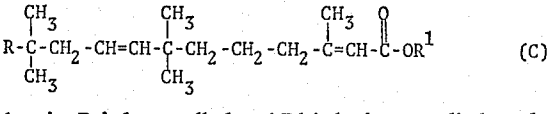
The novel unsaturated quaternary alkyl esters of the present invention and derivatives thereof are represented by the following formulas:



(A)



(B)



(C)

wherein, R is lower alkyl and R^1 is hydrogen, alkyl, cycloalkyl, aralkyl, aryl or a metal.

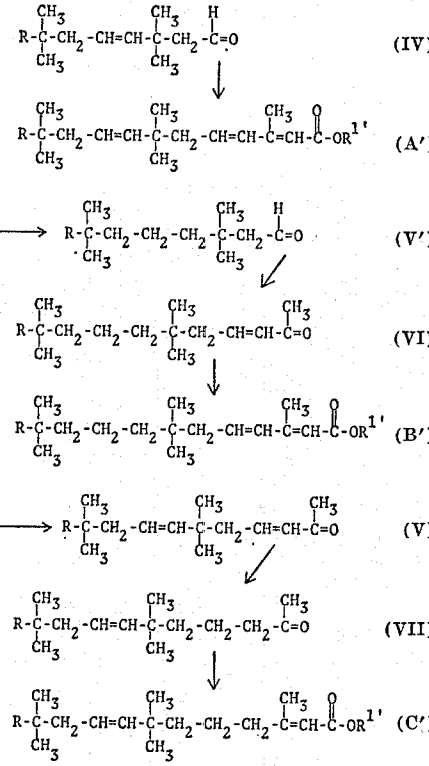
The term "alkyl," as used herein, refers to a straight or branched chain saturated aliphatic hydrocarbon group having a chain length of one to eight carbon atoms. The term "lower alkyl," as used herein, refers to a primary or secondary alkyl group having a chain length of one to six carbon atoms. The term "cycloalkyl," as used herein, refers to a cycloalkyl group of four to eight carbon atoms. The term "aralkyl," as used herein, refers to an aralkyl group of seven to twelve carbon atoms, such as benzyl, phenylethyl, methylbenzyl and naphthylmethyl. The term "aryl," as used herein, refers to an aryl group of six to twelve carbon atoms, such as phenyl, methylphenyl, naphthyl, and the like. The term "metal," as used herein, refers to lithium, sodium, potassium, calcium, strontium, copper and manganese.

The compounds of Formulas A, B and C are useful for the control of insects. The utility of these compounds as insect control agents is believed to be attributable to their juvenile hormone activity. They are preferably applied to the immature insect, namely—during the embryo, larvae or pupae stage in view of their ability to inhibit metamorphosis and otherwise cause abnormal development. These compounds are effective control agents for Hemipteran insects, such as Lygaeidae, Miridae and Pyrrhocoridae; Lepidopteran insects, such as Pyralidae, Noctuidae and Gelechiidae; Coleopteran, such as Tenebrionidae; and Dipteran. The compounds can be applied at low dosage levels of the order of 0.001 μg. to 15.0 μg. per insect. Suitable carrier substances include liquid or solid carriers, such as water, mineral or vegetable oils, talc, vermiculite, natural and synthetic resins and silica. Treatment

of insects in accordance with the present invention is accomplished by spraying dusting or exposing the insects to the vapor of the compounds of Formulas A, B and C. Generally, a concentration of less than 25% of the active compound is employed. The formulations can include insect attractants, emulsifying agents or wetting agents to assist in the application and effectiveness of the active ingredient. In the application of the compounds, there is generally employed a mixture of the C-2,3 trans and cis isomers, the C-2,3 trans isomer being the preferred embodiment for the control of insects.

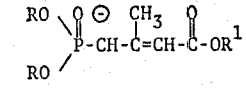
In the description following and hereinafter, each of R and R^1 is defined as hereinabove and $R^{1'}$ is alkyl, cycloalkyl, aryl or aralkyl.

The compounds of the present invention are prepared according to the following outline syntheses.



(IV), (A'), (V'), (VI), (B'), (V), (VII), (C')

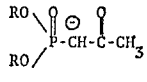
The novel triene esters (A') are prepared by the reaction of the aldehyde (IV) with the carbanion of the Formula VIII:



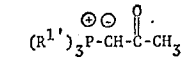
The phosphonate anion (VIII) is generated by treatment of the corresponding phosphonate with base, such as alkali metal hydride or alkali metal alkoxide, e.g. sodium hydride or sodium methoxide, in organic solvent inert to the reaction, such as a hydrocarbon, ether or dialkylsulfoxide solvent, e.g. benzene, toluene, dimethylformamide, tetrahydrofuran, and the like. The reaction is conducted at a temperature of from about −20° C. to room temperature or above. The reaction of the phosphonate anion with the aldehyde is generally conducted at temperature of about 0° C. to room temperature or above. The phosphonate can be prepared as described by Pattenden et al., J. Chem. Soc. (C), 1984 and 1997 (1968). The esters (A') are converted into the corresponding acid (A; R^1 is hydrogen) by hydrolysis with base, such as potassium carbonate or sodium carbonate

in organic solvent, such as methanol or ethanol. Other esters of the present invention can be prepared by transesterification or conversion of the acid into the acid halide by treatment with thionyl chloride, oxalyl chloride, or the like, and then reacting the acid halide with the alcohol corresponding to the ester moiety desired.

In the preparation of the diene esters of formula B', an aldehyde of Formula IV is hydrogenated using palladium on charcoal or other catalyst to yield the saturated aldehyde (V') which is reacted with phosphonate anion of Formula IX using the conditions described above or with an ylid of Formula X to yield the unsaturated ketone (VI).

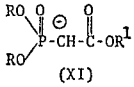


(IX)

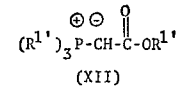


(X)

The unsaturated ketone (VI) is then reacted with a phosphonate anion (XI) to yield to diene ester (B') or by Wittig reaction using the ylid (XII).



(XI)

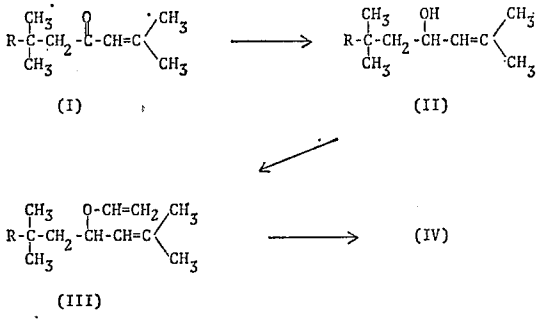


(XII)

Conversion of VI into B' using phosphonate anion can be done using the same conditions as for conversion of IV into A: Wittig reactions are generally done at higher temperatures, such as from room temperature to reflux. The ylids are prepared from the corresponding phosphonium bromide or chloride by treatment with a base, such as butyl lithium, alkali metal hydride, alkali metal hydroxide or alkali metal carbonate in an organic solvent, such as toluene, benzene, or tetrahydrofuran, or water or aqueous organic solvent depending upon the particular base.

In the preparation of the diene esters of Formula C', an aldehyde of Formula IV is reacted with a phosphonate anion (IX) or ylid (X) to obtain the di-unsaturated ketone (V) which is hydrogenated selectively using palladium in basic medium, lithium and liquid ammonia, or the like, to yield the corresponding 3,4-dihydro ketone (VII). Suitable hydrogenation procedures are described by Augustine, "Catalytic Hydrogenation," M. Dekker, New York, pages 60–62 (1965); Augustine, "Reduction," M. Dekker, New York, pages 104–105 (1968) and House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, pages 61–66 (1965). The ketone (VII) is then converted into an ester of formula C' by reaction with a phosphonate anion of Formula XI or an ylid of Formula XII. The esters B' and C' can be hydrolyzed using base to obtain acids of Formulas B and C wherein R^1 is hydrogen.

The aldehydes of Formula IV are prepared according to the following outlined synthesis.



(I) (II) (III) (IV)

The ketone (I), prepared by the alkylation of phorone using an organo-copper complex prepared from lower alkyl lithium or lower alkyl magnesium halide and cuprous iodide, is reduced using lithium aluminum hydride or sodium borohydride to yield the alcohol (II). See Anderson et al., J. Amer. Chem. Soc. 92, 735 (1970) and Siddall et al., J. Amer. Chem. Soc. 91, 1853 (1969). The alcohol (II) is then reacted with a lower alkyl vinyl ether in the presence of mercuric acetate to yield the vinyl ether (III) which upon heating, under inert atmosphere, at a temperature of about 160° C. to about 220° C., generally 180° C. to 210° C., in a sealed vessel yields the unsaturated aldehyde (IV).

The compounds of Formulas IV, V, VI and VII, in addition to their utility as intermediates for the insect control agents of Formulas A, B and C, are useful in chemical syntheses in general, such as the preparation of perfumery additives and as odorants for perfumery compositions. The polyene esters of Formulas A, B and C are useful lubricants and plasticizers for polymers, such as hydrocarbon polymers and chlorinated hydrocarbon polymers.

The following examples are provided to illustrate the present invention. Temperature is given in degrees centigrade.

EXAMPLE 1

(A) To a suspension of cuprous iodide (25 g.) in 500 ml. of dry ether at 0° is added 150 ml. of 1.6 M methyl lithium in ether at a moderate rate with stirring under argon. After about 20 minutes at 0°, 14 g. of phorone in 30 ml. of ether is added slowly and the mixture stirred for about 0.5 hour. The mixture is then poured into rapidly stirred aqueous ammonium chloride (about one liter), allowed to stand and the layers separated. The ether layer is washed with saturated sodium chloride, the water layer is extracted with ether and combined with the ether phase and dried over sodium sulfate and filtered. The filtrate is evaporated in vacuo to yield 2,6,6-trimethylhept-2-en-4-one.

(B) 100 grams of ketone of Part A dissolved in a mixture of 100 ml. of anhydrous ether and 100 ml. of hexane is added dropwise to a suspension of 10 g. lithium aluminum hydride in 500 ml. anhydrous ether at 0°. The mixture is stirred for 90 minutes at 0°, quenched by dropwise addition of water and extracted with ether. The extract is washed with brine and dried. Evaporation of the solvent and distillation of the residue gives 2,6,6-trimethylhept-2-en-4-ol.

(C) 67 grams of alcohol of Part B and 12 g. mercuric acetate (freshly recrystallized from ethanol containing 1% acetic acid) are dissolved in 600 ml. of ethyl vinyl ether and refluxed for eight hours. Another 12 g. mercuric acetate is added and the solution further refluxed overnight. The solution is cooled to 0° and 200 ml. of saturated potassium carbonate is added. After one hour stirring, the organic layer is separated and washed with brine. After evaporation of the solvent, the vinylether (III; R is methyl) is heated in a bomb under nitrogen for one hour at 195°–210°. After cooling to room temperature, the reaction product is filtered in hexane through a short column of Woelm neutral alumina (activity III) and distilled to yield 3,3,7,7-tetramethyloct-4-en-1-al.

(D) The process of Part A is repeated using each of ethyllithium, n-propylithium, i-propylithium and butyllithium in place of methyllithium to yield 2,6,6-trimethyloct-2-en-4-one, 2,6,6-trimethylnon-2 - en - 4 - one, 2,6,6,7-tetramethyloct-2-en-4-one and 2,6,6-trimethyldec-2-en-4-one, respectively, which are reduced according to the procedure of Part B to the corresponding C-4 alcohol of Formula II. Each of the thus-obtained alcohols is reacted with ethyl vinyl ether using the procedure of Part C above to yield the corresponding vinyl ether of Formula III (R is ethyl, n-propyl, i-propyl and n-butyl, respectively). The vinyl ethers are heated using the procedure of Part C above to yield the corresponding aldehyde, that is 3,3,7,7-tetramethylnon-4-en-1-al, 3,3,7,7-tetramethyldec - 4 - en - 1 - al, 3,3,7,7,8-pentamethylnon-4-en-1-al and 3,3,7,7 - tetramethylundec - 4 - en - 1 - al, respectively. Similarly, using n-hexyl lithium in place of methyl

lithium, there is obtained, as the final product, 3,3,7,7-tetramethyltridec-4-en - 1 - al, by the processes of this example.

EXAMPLE 2

Sodium methoxide (from 200 mg. sodium and 12 ml. methanol) is added dropwise to a stirred solution of 1.8 g. of trans diethyl 3-ethoxycarbonyl-2-methylprop-2-enyl phosphonate (VIII; R=R$^{1'}$=ethyl) and 1 g. of 3,3,7,7-tetramethyloct-4-en-1-al in 50 ml. of dimethylformamide under nitrogen. The reaction mixture is left for one hour at room temperature and then water is added followed by extraction with ether. The ethereal extracts are washed with brine, dried and evaporated to yield trans/cis methyl 3,7,7,11,11-pentamethyldodeca-2,4,8 - trienoate. The isomeric mixture can be chromatographed on silica or distilled for purification. The isomeric mixture is predominantly trans at C-2,3.

The foregoing procedure is repeated using sodium ethoxide in place of sodium methoxide to yield trans/cis ethyl 3,7,7,11,11-pentamethyldodeca-2,4,8-trienoate.

The procedure of this example is repeated using sodium ethoxide in place of sodium methoxide and using each of the aldehydes of Example 1 (Part D) in place of 3,3,7,7-tetramethyloct-4-en-1-al to yield trans/cis ethyl 3,7,7,11,11-pentamethyltrideca-2,4,8 - trienoate, trans/cis ethyl 3,7,7,11,11-pentamethyltetradeca - 2,4,8 - trienoate, trans/cis ethyl 3,7,7,11,11,12-hexamethyltridec-2,4,8-trienoate, trans/cis ethyl 3,7,7,11,11-pentamethylpentadeca-2,4,8-trienoate and trans/cis ethyl 3,7,7,11,11-pentamethylheptadeca-2,4,8-trienoate, respectively. Similarly, the corresponding methyl esters are prepared from the aldehydes of Example 1(D) using the process of this example. The trans/cis isomeric mixture of each of the foregoing compounds is separable into the individual isomers using gas-liquid chromatography or fractional distillation.

EXAMPLE 3

To a mixture of 250 mg. of sodium hydride in 2 ml. of tetrahydrofuran, with ice-cooling, is added 1.6 g. of trans diethyl 3-ethoxycarbonyl-2-methylprop-2-enyl phosphonate in 5 ml. of tetrahydrofuran. Temperature is allowed to rise to room temperature and after 30 minutes, 1 g. of 3,3,7,7-tetramethyloct-4-en-1-al is added. After about one hour at room temperature, the mixture is extracted with ether. The ethereal extracts are washed with brine, dried and evaporated to yield trans/cis ethyl 3,7,7,11,11-pentamethyldodeca-2,4,8-trienoate (about 1:1 mixture of C-2,3 trans and cis isomers).

EXAMPLE 4

Two grams of 3,3,7,7,-tetramethyloct-4-en-1-al in 10 ml. of ethanol over 100 mg. of 5% palladium-on-charcoal is hydrogenated overnight. The catalyst is filtered to yield 3,3,7,7-tetramethyloctan-1-al.

EXAMPLE 5

(A) One gram of 5% palladium-on-carbon and 10 g. of 3,3,7,7-tetramethyloct-4-en-1-al is stirred in 50 ml. of ethanol under excess hydrogen at one atmosphere pressure and at room temperature until the theoretical amount of hydrogen is absorbed (about 48 hours). Then, 2 ml. of dichloromethane is added and the mixture filtered. The filtrate is concentrated under reduced pressure to yield 3,3,7,7-tetramethyloctan-1-al.

By use of the foregoing procedure, each of the aldehydes of Example 1(D) is hydrogenated to the corresponding 4,5-dihydro compound.

(B) To 126 mg. of a 57% dispersion of sodium hydride in oil is added pentane. The pentane is removed and the sodium hydride washed several times with pentane. To the washed sodium hydride is added 582 mg. of diethyl acetylmethylphosphonate (IX; R is ethyl) in 5 ml. of tetrahydrofuran at −10° under argon. After several minutes, the solution is transferred to a solution of 500 mg. of 3,3,7,7-tetramethyloctan-1-al in about 4 ml. of dry tetrahydrofuran under argon over a period of about 20 minutes at room temperature. After about two hours, water is added followed by addition of ether and the layers separated. The organic layer is washed with saturated sodium chloride, dried over sodium sulfate and evaporated under reduced pressure to yield 6,6,10,10-tetramethylundec-3-en-2-one.

Similarly, each of 3,3,7,7-tetramethylnonan-1-al, 3,3,7,7-tetramethyldecan-1-al, 3,3,7,7,8-pentamethylnonan - 1-al, 3,3,7,7-tetramethylundecan-1-al and 3,3,7,7-tetramethyltridecan-1-al is converted into 6,6,10,10-tetramethyldodec-3-en-2-one, 6,6,10,10-tetramethyltridec-3-en-2-one, 6,6,10,10,11-pentamethyldodec-3-en - 2 - one, 6,6,10,10-tetramethyltetradec-3-en-2-one and 6,6,10,10-tetramethylhexadec-3-en-2-one, respectively.

By use of the process of this example, other 2-ketones of Formula VI are prepared.

(C) 32.2 grams of sodium hydride (57% in oil) is placed in a dry 1:1, 3-neck flask (fitted with a nitrogen inlet) and washed three times (100 ml. each) with dry pentane under nitrogen, carefully decanting only the solvent each time, into a beaker of ethanol. 400 milliliters dry tetrahydrofuran is then added, the mixture cooled to 0°, and 156.0 g. of diethyl carbethoxymethylphosphonate (XI; R=R$^{1'}$=ethyl) is added under nitrogen. The solution is stirred for 0.5 hour after addition is complete, and then 123.5 g. of 6,6,10,10-tetramethylundec-3-en-2-one in 250 ml. dry tetrahydrofuran over 0.5 hour period at room temperature under nitrogen. The mixture is stirred overnight and then poured into saturated NaCl at 0° and extracted with ether (3× 200 ml.), the organic layers dried ($CaSO_4$) and concentrated under reduced pressure to yield trans/cis ethyl 3,7,7,11,11-pentamethyldodeca-2,4-dienoate which can be separated into the individual C-2,3 trans and cis isomers using gas-liquid chromatography or fractional distillation.

The above process is repeated using each of the 2-ketones of Part B as the starting material to yield trans/cis ethyl 3,7,7,11,11 - pentamethyltrideca - 2,4 - dienoate, trans/cis ethyl 3,7,7,11,11 - pentamethyltetradeca - 2,4-dienoate, trans/cis ethyl 3,7,7,11,11 - hexamethyltrideca-2,4 - dienoate, trans/cis ethyl 3,7,7,11,11 - pentamethylpentadeca - 2,4 - dienoate and trans/cis ethyl 3,7,7,11,11-pentamethylheptadeca-2,4-dienoate, respectively.

By using diethyl carbomethoxymethylphosphonate in the process of Part C, the corresponding 2,4-diene methyl esters are obtained. Similarly, by use of the processes of this example, other esters of Formula B' are obtained.

EXAMPLE 6

(A) The process of Example 5(B) is repeated with the exception of using 3,3,7,7 - tetramethyloct-4-en-1-al in place of 3,3,7,7 - tetramethyloctan - 1 - al to yield 6,6,10,10 - tetramethylundeca - 3,7 - diene - 2 - one. Similarly, each of the mono-unsaturated aldehydes of Example 1(D) are converted into the corresponding di-unsaturated 2-ketones of Formula V, i.e. 6,6,10,10-tetramethyldodeca-3,7 - dien - 2 - one, 6,6,10,10-tetramethyltrideca-3,7-dien-2-one, 6,6,10,10,11-pentamethyldodeca - 3,7 - dien-2-one, 6,6,10,10 - tetramethyltetradeca - 3,7 - dien - 2 - one and 6,6,10,10 - tetramethylhexadeca - 3,7 - dien - 2 - one, respectively.

(B) Each of the di-unsaturated ketones of Part A is reduced using lithium in liquid ammonia to yield the corresponding 3,4-dihydro compound of Formula VII, that is 6,6,10,10 - tetramethylundec-7-en-2-one, 6,6,10,10-tetramethyldodec - 7 - en - 2 - one, 6,6,10,10-tetramethyltridec-7-en-2-one, 6,6,10,10,11-pentamethyldodec-7-en-2-one, 6,6,10,10-tetramethyltetradec-7-en-2-one and 6,6,10,10-tetramethylhexadec-7-en-2-one, respectively.

(C) The 2-ketones of Part B are used as the starting material in the process of Example 5(C) to yield the

corresponding diene esters of Formula C', that is, trans/cis ethyl 3,7,7,11,11 - pentamethyldodeca - 2,8 - dienoate, trans/cis ethyl 3,7,7,11,11 - pentamethyltrideca-2,8-dienoate, trans/cis ethyl 3,7,7,11,11 - pentamethyltetradeca-2,8-dienoate, trans/cis ethyl 3,7,7,11,11,12 - hexamethyltrideca - 2,8 - dienoate, trans/cis ethyl 3,7,7,11,11 - pentamethylpentadeca - 2,8 - dienoate and trans/cis ethyl 3,7,7,11,11 - pentamethylheptadeca - 2,8 - dienoate, respectively. The individual C-2,3 trans and cis isomers can be separated by gas-liquid chromatography or fractional distillation. The corresponding methyl esters are obtained using the diethyl phosphonate anion of Formula XI wherein $R^{1'}$ is methyl.

EXAMPLE 7

A mixture of 1 g. of trans/cis methyl 3,7,7,11,11-pentamethyldodeca-2,4,8-trienoate, 60 ml. of methanol, 0.2 g. of sodium carbonate and 6 ml. of water is stirred at about 30° for about 24 hours. The mixture is then diluted with water, neutralized and extracted with ether. The organic phase is washed with water, dried over sodium sulfate and evaporated to yield trans/cis 3,7,7,11,11-pentamethyldodeca-2,4,8-trienoic acid.

Using the foregoing procedure, the other esters of Formulas A', B' and C' are hydrolyzed to the corresponding free acid.

EXAMPLE 8

One gram of thionyl chloride is added with stirring at room temperature to 0.5 g. of trans/cis 3,7,7,11,11-pentamethyldodeca-2,4,8-trienoic acid and the mixture heated at about 50° for 10 minutes. Excess thionyl chloride is removed by evaporation and then t-butyl alcohol (about 2 equivalents) is added and the mixture heated at about 50° for about five minutes. Excess t-butyl alcohol is removed by evaporation to yield trans/cis t-butyl 3,7,7,11,11 - pentamethyldodeca - 2,4,8 - trienoate which is purified by chromatography.

Similarly, by using other alcohols, such as cyclohexyl alcohol, benzyl alcohol, phenol, n-pentanol, n-hexyl alcohol or i-propanol in the foregoing procedure, the corresponding esters are obtained.

EXAMPLE 9

To a solution of 0.5 g. of trans/cis 3,7,7,11,11-pentamethyldodeca - 2,4,8 - trienoic acid in 15 ml. of benzene is added with stirring an equivalent amount of potassium bicarbonate. The mixture is stirred until the evolution of carbon dioxide ceases and then evaporated to yield potassium 3,7,7,11,11-pentamethyldodeca-2,4,8-trienoate.

Alternatively, acid salts can be prepared by titrating the acid with an organic solution or aqueous organic solution of the desired metal.

EXAMPLE 10

To 1.6 g. of sodium hydride (57% in oil dispersion) in a 500 ml., 3-neck flask, fitted with a nitrogen inlet, is added 25 to 50 ml. of dry hexane or pentane and the mixture swirled under nitrogen. The NaH is allowed to settle and the solvent carefully decanted into a beaker containing ethanol. This rinsing process is repeated twice and 100 ml. dry tetrahydrofuran is added via syringe or pipet. Mixture is cooled in an ice-bath and 9.0 g. triethyl phosphonoacetate (dried over molecular sieves) is added via additional funnel over a 10 minute period. Stir an additional one-half hour. The solution of the above anion is transferred via syringe to a 125 ml. addition funnel (with pressure equalizing arm) and is added over about one hour to 6.73 g. of 6,6,10,10 - tetramethyldodec-7-en-2-one at room temperature with stirring. The homogenous solution is then stirred overnight (18–24 hours). The mixture is then poured into saturated sodium chloride at 0° and extracted with ether. The organic phase is dried and concentrated under reduced pressure to yield trans/cis ethyl 3,7,7,11,11 - pentamethyltrideca - 2,8 - dienoate which can be purified by chromatography or distillation.

EXAMPLE 11

41 grams of 3,3,7,7-tetramethyloct-4-en-1-al and 78.4 g. of recrystallized (ethyl acetate) triphenylphosphineacetylmethylene [Ramirez et al., J. Org. Chem. 22, 41 (1957)] are refluxed in one liter of dry toluene for 18 hours, under nitrogen. Most of the solvent is removed in vacuo, 500 ml. pentane is added and the mixture filtered. The flask and the triphenylphosphine oxide filter cake are washed several times with pentane. The filtrate is concentrated in vacuo to yield 6,6,10,10-tetramethylundeca-3,7-dien-2-one.

By use of the foregoing Wittig reaction, other aldehydes of Formula IV are converted into the corresponding di-unsaturated 2-ketones of Formula VII.

EXAMPLE 12

One gram of triphenylphosphine acetylmethylene and 450 mg. of 3,3,7,7-tetramethylnon-4-en-1-al are dissolved in 10 ml. toluene and refluxed under nitrogen overnight. The toluene is distilled off and the formed triphenylphosphine oxide crystallized by addition of pentane. Filtration and evaporation of the pentane gives a residue, which is further purified by preparative thin-layer chromatography, with the plate eluted with 15% ethyl acetate:hexane. Removal of the UV active band gives 6,6,10,10-tetramethyldodeca-3,7-dien-2-one.

EXAMPLE 13

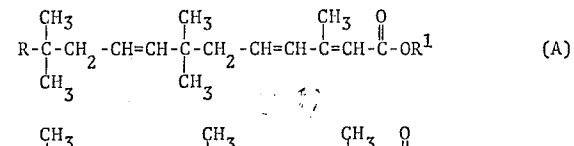
One gram of 6,6,10,10-tetramethylundeca-3,7-dien-2-one in 10 ml. of 0.3 N potassium hydroxide:ethanol over 100 mg. of 5% palladium-on-charcoal is hydrogenated at room temperature and atmospheric pressure, until the theoretical amount of hydrogen is taken up, to yield 6,6,10,10-tetramethylundec-7-en-2-one which is worked up by filtration followed by evaporation under reduced pressure.

EXAMPLE 14

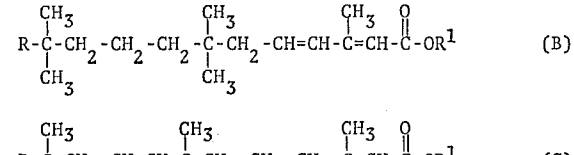
The diene esters (B') can be prepared in one step from the saturated aldehydes (V') by reaction with the phosphonate anions (VIII) using the conditions described herein for conversion of aldehyde IV to the esters A'.

What is claimed is:

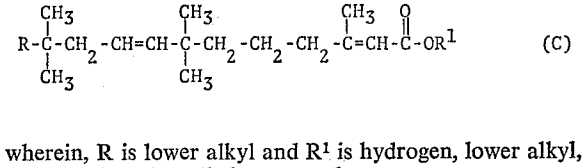
1. A compound selected from those of the following formulas:



(A)



(B)



(C)

wherein, R is lower alkyl and R^1 is hydrogen, lower alkyl, cycloalkyl, aryl, aralkyl or a metal.

2. A compound according to claim **1** wherein the configuration at C-2,3 is trans/cis.

3. A compound according to claim **2** wherein R^1 is lower alkyl.

4. A compound of Formula A according to claim **2**.

5. A compound according to claim **4** wherein R^1 is lower alkyl and R is methyl, ethyl or propyl.

6. A compound according to claim **5** wherein each of R^1 and R is methyl or ethyl.

7. A compound of Formula B according to claim **2**.

8. A compound according to claim 7 wherein R is methyl, ethyl or propyl and R^1 is lower alkyl.

9. A compound according to claim 8 wherein each of R and R^1 is methyl or ethyl.

10. A compound of Formula C according to claim 2.

11. A compound according to claim 10 wherein R is methyl, ethyl or propyl and R^1 is lower alkyl.

12. A compound according to claim 11 wherein each of R and R^1 is methyl or ethyl.

13. A compound according to claim 2 wherein R^1 is hydrogen, lower alkyl of one to four carbons, benzyl, cyclopentyl or cyclohexyl.

References Cited

UNITED STATES PATENTS

3,177,226 4/1965 Stilz et al. ---------- 260—340.5

OTHER REFERENCES

Chemical Abstracts, vol. 68, 95597r (1968).

LEWIS GOTTS, Primary Examiner

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U.S. Cl. X.R.

252—56 S, 522; 260—31.2 R, 410, 410.5, 413, 593 R, 601 R, 606.5 F, 614 R, 941; 424—312, 315.