

UNITED STATES PATENT OFFICE

2,669,579

PREPARATION OF DIACYLOXYDECADIENES

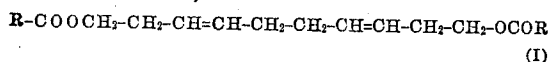
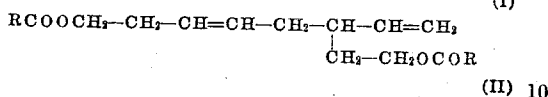
Richard S. Urban, Philadelphia, Pa., assignor to
Rohm & Haas Company, Philadelphia, Pa., a
corporation of Delaware

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Serial No. 319,408

10 Claims. (Cl. 260—488)

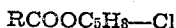
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This invention relates to—and has for its object—a process for the preparation of mixtures of isomeric diacyloxydecadienes, which have the general formulas,



in which R represents a hydrogen atom or a methyl group or an ethyl group.

The process comprises reacting finely divided iron with a chloropentenyl ester or a mixture of isomeric chloropentenyl esters, having the general formula,



in which R, as above, is a hydrogen atom or a methyl or ethyl group. The products of the reaction are iron chloride and a mixture of isomeric diacyloxydecadienes having the above general formulas.

The chloropentenyl esters which are essential reactants in the process of this invention are themselves prepared most conveniently by reacting butadiene, hydrogen chloride, formaldehyde and either formic, acetic or propionic acid in the presence of an acidic catalyst according to the process described in application for Letters Patent, Serial No. 319,407, filed of even date. That process gives rise to mixtures of isomeric chloropentenyl esters which can be separated and then subjected individually to the process of this invention. Alternatively, mixtures of the isomeric esters can be employed in the instant process. In all cases, however, a mixture of the two isomeric diacyloxydecadienes is obtained, even when the starting material is a single chloropentenyl ester. Furthermore, the straight-chain diacyloxydecadiene (I, above) is always formed in predominant amount.

The reaction of a chloropentenyl ester with finely divided iron is carried out at a temperature from about 10° C.—or preferably 20° C.—to the refluxing temperature of the reaction mixture.

The use of a solvent is strongly recommended in order to facilitate the reaction. Alcohols, in general, are good solvents and of these ethanol appears to be most satisfactory. The use of other alcohols has been studied and it has been found that those containing one to seven carbon atoms, such as butyl, hexyl and benzyl alcohols, have an advantage over the higher alcohols in that they can be more readily and cleanly separated from the reaction mixture by distillation. Other pre-

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ferred solvents include acetonitrile, dimethylformamide, propionitrile, butyronitrile and dioxane.

The iron should be in a finely divided form. While coarse metal filings can be used, it is found that the yield of the diacyloxydecadienes is relatively low and the yield of by-products is objectionably high. Therefore, in order to assure best results, the iron should be so finely divided as to pass through a No. 140 U. S. Standard sieve. Since the oxides of iron inhibit the reaction, it is most desirable that the metal be pure. Pyrophoric or hydrogen-reduced iron is recommended. At least one-half mole of iron is employed per mole of chloropentenyl ester and, in fact, it is advantageous to use an excess of the order of 10–50%. The maximum amount of iron which can be used is limited only by considerations of economy and mechanical operation.

It has also been found that the rate of reaction can be increased and the quantity of by-products can be reduced when a finely divided metal or a salt of a metal which is below iron in the electromotive series is employed. In view of the influence which these materials exert in conjunction with the iron coupling agent, they are called activators.

The metals which are employed as such or in the form of salts together with the iron and which are below iron in the electromotive series are cadmium, cobalt, nickel, tin, lead, palladium, copper, mercury, silver, gold and platinum. While all of these serve as activators in the instant invention in conjunction with iron, it is preferred for reasons of economy and efficiency to employ metallic copper, nickel, cobalt and mercury and the salts of these elements. All of the salts of the metals listed above are operable—that is, the water-soluble or the water-insoluble salts of organic and inorganic acids. Actually, the salts of the strong inorganic acids, typified by chlorides, sulfates, nitrates and phosphates are preferred but others such as acetates, formates, oxalates, benzoates and phthalates can be used.

The amount of the activator should be within the range of 1 to 15%—or preferably 2 to 8%—calculated as metal and based on the weight of the iron. Thus if a salt is employed, that amount of the salt is taken which provides 1 to 15% of the metal in the salt, based on the iron.

The reaction can be carried out under normal, super-, or sub-atmospheric pressure; but for reasons of efficiency it is preferred to employ normal or superatmospheric pressures.

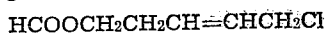
The following examples, in which all parts are

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by weight, serve to illustrate the process of this invention.

Example 1

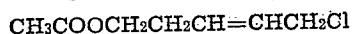
A mixture of 120 parts of acetonitrile, 25 parts of hydrogen-reduced iron powder (Mallinckrodt), 5 parts of hydrated nickel sulfate, and 74.3 parts (0.5 mole) of chloropentenyl formate was stirred and heated at refluxing temperature for two hours. The chloropentenyl formate was the isomer having the formula,



At the end of this time, the grey color of the reaction mixture gradually turned green and heating was continued for three more hours. Then 200 parts of water was added. After cooling, the organic layer was taken up in 100 parts of ether. The ether solution was washed with water, dried and fractionally distilled. The fraction which boiled at 114°-122° C./0.5 mm. weighed 36 parts and represented a 64% yield of a mixture of diformoxydecadienes, whose composition was confirmed by analysis. The straight-chain isomer, conforming to general formula I above, was present to the extent of about three times the amount of the other isomer conforming to general formula II above. The product was hydrogenated and saponified to yield 74.3% of the theoretical amount of decamethylene glycol (M. P. 70°-72° C.).

Example 2

By the procedure of Example 1 above, a mixture of 74.8 parts (0.46 mole) of chloropentenyl acetate, having the formula



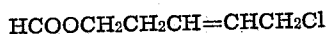
24 parts of hydrogen-reduced iron powder, 120 parts of acetonitrile and 0.5 part of nickel sulfate was refluxed for five hours, extracted with ether and fractionally distilled. In this manner, a 69.5% yield was obtained of a mixture of diacetoxydecadienes which boiled at 120°-155° C./0.6 mm. Here again the amount of straight-chain decadiene predominated. The composition of the product was confirmed by analysis; and after being hydrogenated and saponified, the product gave a 75% yield of decamethylene glycol (M. P. 71°-74° C.).

Example 3

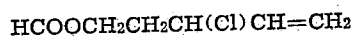
By the same procedure, a 69% yield of a mixture of dipropoxydecadienes was obtained from chloropentenyl propionate.

Example 4

The procedure described in Example 1 above was followed several times with one exception, namely, that 74.3 parts (0.5 mole) of a mixture of isomeric chloropentenyl formates, having the formulas



and

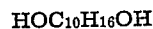


was used. In all cases, the yield of the mixture of diformoxydecadienes was between 60 and 80%.

As shown above, the diacyloxydecadienes are readily converted into glycols, predominantly decamethylene glycol. The decamethylene glycol in turn is easily oxidized to sebacic acid. Thus, the products of this invention constitute an excellent source of dihydric alcohols and dicarboxylic acids, all of which are widely used for the manufacture of organic plasticizers, alkyl resins and linear polyesters. Furthermore, the

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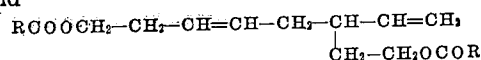
diacyloxydecadienes and mixtures of their isomers can be saponified to produce isomeric unsaturated glycols of the general formula,



particularly 3,7-decadiene-1,10-diol, which are believed to be new compounds.

I claim:

1. A process for preparing a mixture of isomeric diacyloxydecadienes having the formulas, $\text{R}-\text{COOCH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{OCOR}$ and



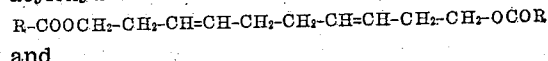
in which R is a member of the class consisting of a hydrogen atom, a methyl group and an ethyl group, which comprises reacting a chloropentenyl ester of the formula,



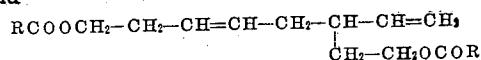
in which R has the significance described above, in the presence of a solvent for the chloropentenyl ester, with finely divided iron at a temperature from 10° C. to the refluxing temperature of the reaction mixture, said iron being present in an amount equal to at least one-half mole per mole of said chloropentenyl ester.

2. The process of claim 1 in which the iron is so finely divided as to pass through a No. 140 U. S. Standard sieve.

3. A process for preparing a mixture of diacyloxydecadienes having the formulas,



and

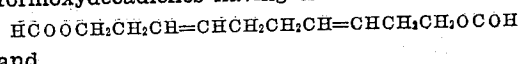


in which R is a member of the class consisting of a hydrogen atom, a methyl group and an ethyl group, which comprises reacting a chloropentenyl ester of the formula,

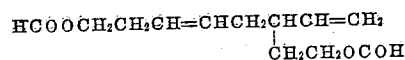


in which R has the significance described above with finely divided iron at a temperature from 10° C. to the refluxing temperature of the reaction mixture in the presence of a solvent for the chloropentenyl ester and an activator, said iron being present in an amount equal to at least one-half mole per mole of said chloropentenyl ester and said activator being a member of the class consisting of (a) the metals below iron in the electromotive series and (b) the salts of said metals and strong inorganic acids and said activator being present in such an amount as to provide 1-15% metal based on the weight of said iron.

4. A process for preparing a mixture of diformoxydecadienes having the formulas



and



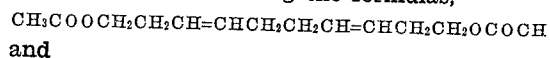
which comprises reacting a chloropentenyl formate of the formula,



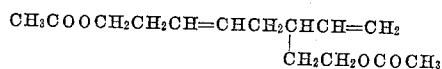
in the presence of a solvent for the chloropentenyl formate with finely divided iron at a temperature from 10° C. to the refluxing temperature of the reaction mixture, said iron being present in an amount equal to at least one-half mole per mole of said chloropentenyl formate.

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5. A process for preparing a mixture of diacetoxydecadienes having the formulas,



and

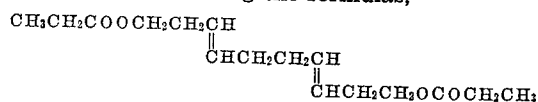


which comprises reacting a chloropentenyl acetate of the formula,

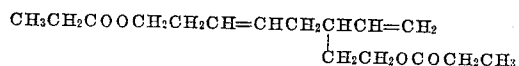


in the presence of a solvent for the chloropentenyl acetate with finely divided iron at a temperature from 10° C. to the refluxing temperature of the reaction mixture, said iron being present in an amount equal to at least one-half mole per mole of said chloropentenyl acetate.

6. A process for preparing a mixture of dipropoxydecadienes having the formulas,



and



which comprises reacting a chloropentenyl propionate of the formula,

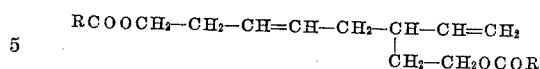


in the presence of a solvent for the chloropentenyl propionate with finely divided iron at a temperature from 10° C. to the refluxing temperature of the reaction mixture, said iron being present in an amount equal to at least one-half mole per mole of said chloropentenyl propionate.

7. As a new composition of matter, a mixture of isomeric diacyloxydecadienes having the formulas,

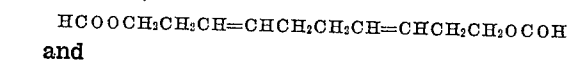
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R-COOCH₂-CH₂-CH=CH-CH₂-CH₂-CH=CH-CH₂-CH₂-OCOR and

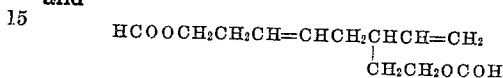


in which R, in all occurrences, is the same member of the class consisting of a hydrogen atom, a methyl group and an ethyl group.

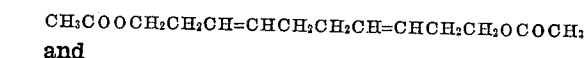
8. As a new composition of matter, a mixture of the isomeric diformoxydecadienes having the formulas,



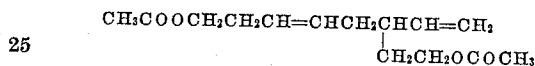
and



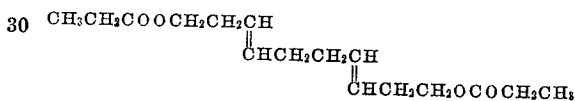
9. As a new composition of matter, a mixture of the isomeric diacetoxycadadienes having the formulas



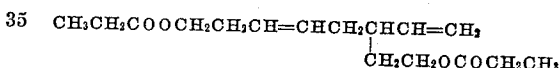
and



10. As a new composition of matter, a mixture of the isomeric dipropoxydecadienes having the formulas



and



RICHARD S. URBAN.

No references cited.