

PATENT SPECIFICATION

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(54) PREPARATION OF GAMMA-PYRONES

(71) We, PFIZER INC., a Corporation organized under the laws of the State of Delaware, United States of America, of 235 East 42nd Street, New York, State of New York, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of gamma-pyrones and particularly to a process for the preparation of gamma-pyrones from intermediate compounds which are derived from furfural. The invention is also concerned with novel intermediate compounds used in the said process.

In one embodiment of the invention maltol (2 - methyl - 3 - hydroxy - gamma - pyrone) is prepared from furfural through intermediates (a) 1 - (2 - furyl) - 1 - ethanol; (b) 2 - (1 - hydroxyethyl) - 2,5 - dialkoxy - 2,5 - dihydrofuran; (c) alkoxy - 2 - methyl - 2H - pyran - 3(6H) - one; and (d) 2 - alkoxy - 4 - methyl - 3,7 - dioxabicyclo[4.1.0]heptan - 5 - one.

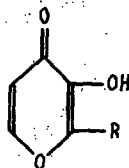
In other embodiments pyromeconic acid (3-hydroxy-gamma-pyrone), ethyl maltol (3-hydroxy-2-ethyl-gamma-pyrone) and other valuable 2-substituted-3-hydroxy-gamma-pyrones are prepared in an analogous manner from furfural.

Maltol is a naturally occurring substance found in the bark of young larch trees, pine needles and chicory. Early commercial production was from the destructive distillation of wood. Synthesis of maltol from 3 - hydroxy - 2 - (1 - piperidylmethyl) - 1,4 - pyrone was reported by Spielman and Freifelder in J. Am. Chem. Soc. 69, 2908 (1947). Schenck and Spielman, J. Am. Chem. Soc. 67, 2276 (1946), obtained maltol by alkaline hydrolysis of streptomycin salts. Chawla and McGonigal, J. Org. Chem. 39, 3281 (1974), and Lichtenthaler and Heidel, Angew. Chem. 81, 999 (1969), reported the synthesis of maltol from protected carbohydrate derivatives.

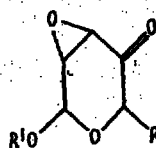
Syntheses of gamma-pyrones such as pyromeconic acid, maltol, ethyl maltol and other 2-substituted-3-hydroxy-gamma-pyrones are described in United Kingdom Patent Specifications No. 1,033,511, 1,033,512, 1,033,513, 1,057,446 and 1,173,383.

Maltol and ethyl maltol enhance the flavour and aroma of a variety of food products. In addition, these materials are used as ingredients in perfumes and essences. The pyromeconic acid derivatives disclosed in United Kingdom Patent Specification No. 1,057,446 inhibit the growth of bacteria and fungi and are useful as flavour and aroma enhancers in foods and beverages and aroma enhancers in perfumes.

In accordance with the present invention there is provided a process for preparing a gamma-pyrone of the general formula:



wherein R is a hydrogen atom, an alkyl group of 1 to 6 carbon atoms, an alkenyl group of 2 to 6 carbon atoms or a phenyl or benzyl group, which comprises reacting a compound of the general formula:—

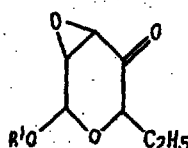


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wherein R is as defined above and R' is an alkyl group of 1 to 6 carbon atoms with an aqueous acid solution.

The aqueous acid solution used in the above process is preferably derived from sulphuric acid, hydrochloric acid, boron trifluoride etherate, *p*-toluenesulphonic acid, formic acid, zinc chloride or tin tetrachloride.

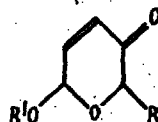
Certain of the intermediate compounds of formula 4 are novel compounds and accordingly the present invention also provides a compound of the form formula:—



4A

wherein R' is an alkyl group of 1 to 6 carbon atoms.

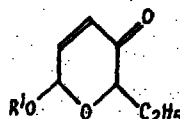
The intermediate compound of formula 4 above is preferably prepared by reacting a compound of the general formula:—



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wherein R and R' are as defined above, with hydrogen peroxide.

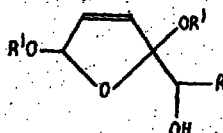
Certain of the intermediate compounds of formula 3 are novel compounds and our Patent Application No. 43608/76, Serial No. 1,505,029, describes and claims a compound of the formula:—



3A

wherein R' is an alkyl group of 1 to 6 carbon atoms.

The intermediate compound of formula 3 above is preferably prepared by reacting a compound of the general formula:—

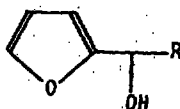


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wherein R and R' are as defined above with a substantially anhydrous acid.

The substantially anhydrous acid used in the above reaction is preferably formic acid, trifluoroacetic acid, *p*-toluenesulphonic acid, methanesulphonic acid, citric acid, oxalic acid, chloroacetic acid, sulphuric acid, hydrochloric acid or phosphoric acid.

The intermediate compound of formula 2 above is preferably prepared by reacting a compound of the formula:—



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wherein R is as defined above, with an alcoholic (R'OH) solution of chlorine or bromine.

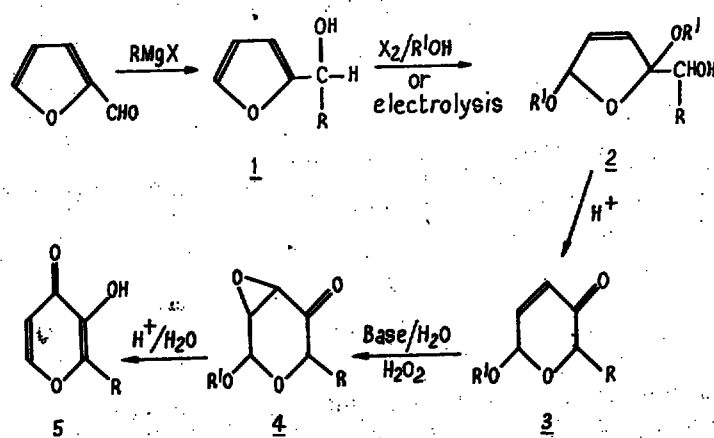
The intermediate compound 1 may be prepared by reacting furfural with a

Grignard reagent of the formula RMgX wherein R is as defined above and X is chlorine or bromine.

Thus the invention provides a process for the preparation of 2-substituted-3-hydroxy-gamma-pyrones involving a series of steps utilizing furfural as the initial starting material. Furfural is an inexpensive raw material which is prepared industrially from pentosans which are contained in cereal straws and brans.

As used herein, the term "alkyl" means both straight and branched chain alkyl groups containing from one to six carbon atoms; the term "alkenyl" means straight and branched chain alkenyl groups containing from two to six carbon atoms; the term "aryl" denotes a monocyclic aromatic hydrocarbon of six to eight carbon atoms; and the term "aralkyl" encompasses alkyl groups in which aryl as defined above is substituted for a hydrogen atom.

The reactions involved in the present invention are illustrated in the following reaction scheme:



wherein R and R' are as defined above and X is chlorine or bromine.

Intermediates: $\text{R}' = \text{alkyl}$
 $\text{R} = \text{hydrogen, alkyl, aryl, alkenyl, aralkyl}$
 Final Product (5): $\text{R} = \text{hydrogen, alkyl, alkenyl, aryl, aralkyl}$
 $\text{R} = \text{H, pyromeconic acid}$
 $\text{R} = \text{CH}_3, \text{ maltol}$
 $\text{R} = \text{CH}_2\text{CH}_3, \text{ ethyl maltol}$

The reaction of furfural with the appropriate Grignard reagent (RMgX) is described in Chemical Abstracts 44, 1092d (1949).

The preparation of intermediate 2 ($\text{R} = \text{H}$) by electrolysis in methanol is described in United Kingdom Patent Specification No. 682736 and Acta Chem. Scand 6, 545 (1952). The synthesis employing bromine in methanol is reported in Ann 516, 231 (1935). The reaction using chlorine in an alcoholic solvent is disclosed, for example, in United Kingdom Patent Specification No. 595041. It has been found that the reaction of intermediate 1 with chlorine in an alcoholic solvent at a temperature from -70° to 50°C gives a clean conversion to the desired intermediate 2 with the HCl by-product being neutralized by a base such as ammonia, sodium carbonate or other alkali metal base. The process of the present invention results in yields in excess of 90%.

Intermediate 2 ($\text{R} = \text{CH}_3$) is described in Acta Chem Scand 9, 17 (1955); and Tetrahedron 27, 1973 (1971). Intermediate 2 ($\text{R} = \text{CH}_2\text{CH}_3$) is a new compound which may be made by methods already described.

The reaction of intermediate 2 with a strong organic acid is novel and it produces the desired 6-alkoxy derivative 3 directly in high yield and avoids the formation of the corresponding hydroxy derivative which is very unstable to further reactions. Intermediate 2 is contacted with a substantially anhydrous acid. The presence of a protic solvent such as an alcohol or a small amount of water is actually beneficial. Following this reaction, the product, in a state of purity suitable for conversion to intermediate 3, is separated from the acid medium by conventional extraction techniques. Although formic and trifluoroacetic acids are preferred, any acid with

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a pKa of 4 or below will convert intermediate 2 to the desired intermediate 3. Other suitable organic acids include *p*-toluenesulphonic acid, methanesulphonic acid, citric acid, oxalic acid and chloroacetic acid; suitable mineral acids include sulphuric acid, hydrochloric acid and phosphoric acid. Acidic resins such as "Amberlite" GC-120 and "Dowex" 50W also may be employed. The words "Amberlite" and "Dowex" are registered Trade Marks.

The epoxidation of intermediate 3 to the epoxy ketone 4 is a novel process. The intermediate 3 is dissolved in a suitable solvent such as water or an alcohol, such as isopropyl alcohol or methanol. A base such as sodium bicarbonate or sodium hydroxide is added followed by the addition of hydrogen peroxide (30%). The desired intermediate 4 may be separated by conventional extraction techniques, and is suitable for rearrangement to the desired pyrone 5 without further purification.

The final rearrangement of the epoxy ketone 4 to the gamma-pyrone 5 is novel and proceeds in good yield and purity. The intermediate 4 is reacted in an acidic medium and subsequent isolation of the desired gamma-pyrone 5 is effected by conventional crystallization or extraction techniques. The pure gamma-pyrone may be recrystallized from an appropriate solvent such as isopropanol, methanol or water. Although hot aqueous mineral acid, such as sulphuric acid or hydrochloric acid, is the most convenient reagent for converting intermediate 4 to product 5, the desired gamma-pyrone may be produced by Lewis acids such as boron trifluoride etherate, zinc chloride or tin tetrachloride; by acidic ion resins such as "Amberlite" GC-120 or "Dowex" 50W; or by strong organic acids such as *p*-toluenesulphonic acid or formic acid.

Compounds related to intermediate 3 ($R=CH_2OH$ or $R=CH_2O-Alkyl$) may be prepared from carbohydrate sources as described in Accounts of Chemical Research 8, 192 (1975). These compounds may be converted to intermediate 4 and product 5 where $R=CH_2OH$ or $CH_2O-Alkyl$. Product 5 ($R=CH_2OH$ or $CH_2O-Alkyl$) may be converted to maltol as described in United Kingdom Specification No. 1,033,511 or Angew Chem 81, 998 (1969).

The following Examples illustrate the invention and the manner in which it may be performed.

EXAMPLE 1

To a 3 neck-roundbottom flask equipped with a magnetic stirring bar, a jacketed addition funnel, a thermometer and a dry ice condenser were added 22.4 g (0.2 mol) of intermediate 1 ($R=CH_3$), 100 ml of methanol and 21.1 g (0.2 mol) of sodium carbonate, and this mixture was cooled to 0°C using an ice-acetone bath. To this rapidly stirred solution was then added dropwise a cold (-30°C) solution of chlorine (11.0 ml, 0.24 mol) in methanol. The addition of chlorine was controlled to keep the reaction temperature under 40°C. The addition required about 2 hours. After the addition, the reaction mixture was stirred at ice bath temperature for 30 minutes, and then allowed to warm to room temperature. The resulting slurry was filtered, the methanol removed *in vacuo*, the residue taken up in benzene and passed through an alumina plug as a final filter. Removal of the benzene provided 31.9 g (91%) of the desired dimethoxy dihydrofuran 2 ($R=CH_3$, $R'=CH_3$). This material can be used without further purification or it can be distilled, b.p. 76-78°/5 mm [104-107°/10-11 mm, Acta Chem. Scand. 9, 17 (1955)].

Analysis:

	C	H
Calc'd. for $C_8H_{10}O_4$:	55.22	8.11
Found:	55.34	8.04

EXAMPLE 2

The method of Example 1 was repeated with intermediate 1 ($R=H$) to yield intermediate 2 ($R=H$, $R'=CH_3$), b.p. 80-82°/5 mm [71°/1.0 mm, Tetrahedron 27, 1973 (1971)].

EXAMPLE 3

The method of Example 1 was repeated with intermediate 1 ($R=CH_2CH_3$) to yield intermediate 2 ($R=CH_2CH_3$, $R'=CH_3$) b.p. 102°/10 mm.

Analysis:

	C	H
Calc'd. for $C_9H_{12}O_4$:	57.50	8.58
Found:	57.39	8.59

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EXAMPLE 4

The method of Example 1 was repeated using intermediate 1 ($R=CH_3$) replacing methanol with isopropanol to yield intermediate 2 [$R=CH_3$, $R'=CH(CH_3)_2$], b.p. 62–64°/0.05 mm.

EXAMPLE 5

The method of Example 1 may be repeated using bromine instead of chlorine using intermediate 1 to yield intermediate 2 where R is hydrogen, methyl, ethyl, hexyl, phenyl, benzyl, vinyl, 1-butenyl, allyl and 1-hexenyl; and R' is methyl, ethyl, isopropyl and hexyl.

EXAMPLE 6

In a small glass electrolysis vessel having a carbon anode and nickel cathode were placed 50 ml of methanol, 0.5 ml of concentrated sulfuric acid, and 1.12 g (0.01 mol) of the intermediate 1 ($R=CH_3$, $R'=CH_3$) and the solution was cooled to -20°C. An electrolysis was then carried out using a potentiostat/galvanostat Princeton Applied Research Corporation Model 373 instrument set to deliver a constant current of 0.6 amperes. After a reaction time of 30 minutes, the reaction was poured into water and the product 2 ($R=CH_3$, $R'=CH_3$), isolated by a chloroform extraction procedure. This procedure is similar to that described in United Kingdom Patent Specification No. 682,736 with sulphuric acid replacing ammonium bromide as the electrolyte.

EXAMPLE 7

The method of Example 6 may be repeated with intermediate 2 to yield intermediate 3 where R is hydrogen, ethyl, hexyl, phenyl, benzyl, vinyl, allyl, 1-butenyl and 1-hexenyl; and R' is ethyl, isopropyl and hexyl.

EXAMPLE 8

To a 2-liter, 3-neck roundbottom flask equipped with a magnetic stirrer, dropping funnel and a thermometer were added 400 ml of formic acid and 20 ml of methanol. To this solution was added a solution of intermediate 2 ($R=CH_3$, $R'=CH_3$) 104.4 g, 0.6 mol in 40 ml of methanol. The dropwise addition required 15 minutes. The reaction was poured in a liter of water and extracted 3 times with 500 ml portions of chloroform. The combined chloroform washings were washed with a sodium bicarbonate aqueous solution and with brine. The chloroform solution was evaporated to a crude yield of 76 g (89%) of intermediate 3 ($R=CH_3$, $R'=CH_3$) as a light brown product. The crude material may be used as such or distilled at 2 mm pressure, 50–52°C. [82–85°/30 mm, Tetrahedron 27, 1973 (1971)].

EXAMPLE 9

The method of Example 8 was repeated with analogous intermediate 2 ($R=H$, $R'=CH_3$) to yield intermediate 3 ($R=H$, $R'=CH_3$), b.p. 60–66°/14 mm [76–81°/23 mm, Tetrahedron 27, 1973 (1971)].

EXAMPLE 10

The method of Example 8 was repeated with intermediate 2 ($R=CH_2CH_3$, $R'=CH_3$) to yield intermediate 3 ($R=CH_2CH_3$, $R'=CH_3$), b.p. 79–80°/14 mm.

EXAMPLE 11

The method of Example 8 may be repeated with intermediate 2 to yield intermediate 3 where R is hexyl, phenyl, benzyl, vinyl, allyl, 1-butenyl and 1-hexenyl; and R' is isopropyl and hexyl.

EXAMPLE 12

The method of Example 8 may be repeated, with comparable results, replacing formic acid with an organic acid selected from citric acid, oxalic acid, chloroacetic acid, p-toluenesulfonic acid, methanesulfonic acid and trifluoroacetic acid.

EXAMPLE 13

In a 3-neck roundbottom flask equipped with an addition funnel, low temperature thermometer and stirring bar was prepared a solution of 5.0 g (0.029 mol) of intermediate 2 ($R=CH_3$, $R'=CH_3$) in diethyl ether (10 ml) and the solution was cooled to -40°C. To this solution was then added dropwise 1.6 ml of concentrated sulfuric acid and the black mixture stirred for 5 minutes at -40°C, poured into water

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and the desired intermediate 3 ($R=CH_3$, $R'=CH_3$) isolated by the method of Example 8.

Substantially the same results may be obtained replacing sulfuric acid with hydrochloric or phosphoric acids.

EXAMPLE 14

To a dry flask was added 1.05 grams (0.0074 mol) of intermediate 3 ($R=CH_3$, $R'=CH_3O$) dissolved in 20 ml of isopropyl alcohol and the flask cooled to $0^\circ C$. Then 0.5 g (0.0059 mol) of sodium bicarbonate and 2.0 ml (0.023 mol) of 30% hydrogen peroxide were added, and the reaction allowed to stir at room temperature for about 2 hours. The reaction mixture was poured into 100 ml of water and the water extracted with chloroform, followed by concentration to yield 0.90 grams (77%) of intermediate 4 ($R=CH_3$, $R'=CH_3$) as a yellow oil which could be distilled at $70-90^\circ/3$ mm. An analytic sample was purified by gas chromatography.

Analysis:

	C	H
Calc'd. for $C_7H_{10}O_4$:	53.16	6.37
Found:	52.90	6.27

EXAMPLE 15

The method of Example 14 was repeated with intermediate 3 ($R=H$, $R'=CH_3$) to yield intermediate 4 ($R=H$, $R'=CH_3$).

Analysis:

	C	H
Calc'd. for $C_6H_8O_4$:	50.00	5.59
Found:	50.09	5.81

EXAMPLE 16

The method of Example 14 was repeated with intermediate 3 ($R=CH_2CH_3$, $R'=CH_3$) to yield intermediate 4 ($R=CH_2CH_3$, $R'=CH_3$).

Analysis:

	C	H
Calc'd. for $C_8H_{12}O_4$:	55.81	7.02
Found:	55.95	7.04

EXAMPLE 17

The method of Example 14 may be repeated with intermediate 3 to yield intermediate 4 where R is hexyl, phenyl, benzyl, vinyl, allyl, 1-butenyl and 1-hexenyl; and R' is isopropyl and hexyl.

EXAMPLE 18

To a 75 ml flask was added 2.84 g (0.02 mol) of intermediate 3 ($R=CH_3$, $R'=CH_3$), 10 ml of water and 10 ml of isopropanol. The solution was cooled to $0-5^\circ C$, and the pH adjusted to 7.0-9.0 with 1 N NaOH. Then 2.1 ml of 30% hydrogen peroxide was added dropwise, with NaOH also added as necessary to maintain constant pH. Cooling was necessary to keep the pot temperature below $10^\circ C$. After the addition of peroxide, the reaction was stirred at $8-10^\circ C$ for about one hour, poured in water and the solution extracted with chloroform. Solvent removal yielded 2.99 g (94.5%) of the intermediate 4 ($R=CH_3$, $R'=CH_3$) as a clear oil. Reaction temperatures above $15^\circ C$ and a pH above 9.5 or below 6.5 result in lower yields of intermediate 4.

Substantially the same results are obtained replacing isopropanol with water.

EXAMPLE 19

To a flask with a condenser was added 3.7 g (0.023 mol) of intermediate 4 ($R=CH_3$, $R'=CH_3$) and 50 ml of 2 M H_2SO_4 . After heating this two phase solution for 1.5 hours at reflux, the reaction mixture was cooled, adjusted to pH 2.2 with 6 N NaOH, extracted 3 times with 100 ml volumes of chloroform and the combined solvent extract concentrated to yield product 5 ($R=CH_3$, maltol).

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EXAMPLE 20

The method of Example 19 may be repeated with intermediate 4 where R is hydrogen, ethyl, hexyl, phenyl, benzyl, allyl, vinyl, 1-butenyl and 1-hexenyl; and R' is methyl, ethyl, isopropyl and hexyl to yield product 5 where R is hydrogen, ethyl, hexyl, phenyl, benzyl, allyl, vinyl, 1-butenyl and 1-hexenyl.

EXAMPLE 21

To a 250 cc Wheaton pressure bottle was added 3.16 g (0.02 mol) of intermediate 4 ($R=CH_3$, $R'=CH_3$) and 50 cc of 2 M H_2SO_4 . The vessel was sealed and heated to 140—160° for 1—2 hours. After cooling, the reaction was processed as in Example 19 to yield maltol ($R=CH_3$).

EXAMPLE 22

The method of Examples 19 and 20 may be repeated, with comparable results, replacing sulfuric acid with hydrochloric acid, Dowex 50W or Amberlite GC-120.

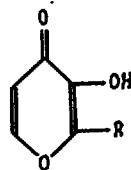
EXAMPLE 23

To a small flask was added 1.58 g (0.01 mol) of intermediate 4 ($R=CH_3$, $R'=CH_3$) and 25 ml of benzene followed by 3.7 ml of boron trifluoride etherate. After stirring for 24 hours at 25°C, the solvent was removed, the residue extracted with chloroform, and the chloroform removed to yield maltol ($R=CH_3$).

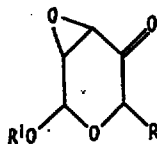
Substantially the same results are obtained when boron trifluoride etherate is replaced with p-toluenesulfonic acid, formic acid, zinc chloride or tin tetrachloride.

WHAT WE CLAIM IS:—

1. A process for preparing a gamma-pyrone of the general formula:—



wherein R is a hydrogen atom, an alkyl group of 1 to 6 carbon atoms, an alkenyl group of 2 to 6 carbon atoms or a phenyl or benzyl group, which comprises reacting a compound of the general formula:—



wherein R is as defined above and R' is an alkyl group of 1 to 6 carbon atoms with an aqueous acid solution.

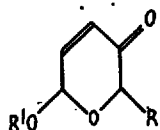
2. A process according to claim 1, wherein the acid solution is derived from sulphuric acid, hydrochloric acid, boron trifluoride etherate, p-toluenesulphonic acid, formic acid, zinc chloride or tin tetrachloride.

3. A process according to claim 1 or 2, wherein the gamma-pyrone of formula 5 is 2-methyl-3-hydroxy gamma-pyrone.

4. A process according to claim 1 or 2, wherein the gamma-pyrone of formula 5 is 2-ethyl-3-hydroxy-gamma-pyrone.

5. A process according to claim 1 or 2, wherein the gamma-pyrone of formula 5 is 2-vinyl-3-hydroxy-gamma-pyrone.

6. A process according to claim 1, wherein the compound of formula 4 is prepared by reacting a compound of the general formula:





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EXAMPLE 20

The method of Example 19 may be repeated with intermediate 4 where R is hydrogen, ethyl, hexyl, phenyl, benzyl, allyl, vinyl, 1-butenyl and 1-hexenyl; and R' is methyl, ethyl, isopropyl and hexyl to yield product 5 where R is hydrogen, ethyl, hexyl, phenyl, benzyl, allyl, vinyl, 1-butenyl and 1-hexenyl.

EXAMPLE 21

To a 250 cc Wheaton pressure bottle was added 3.16 g (0.02 mol) of intermediate 4 ($R=CH_3$, $R'=CH_3$) and 50 cc of 2 M H_2SO_4 . The vessel was sealed and heated to 140–160° for 1–2 hours. After cooling, the reaction was processed as in Example 19 to yield maltol ($R=CH_3$).

EXAMPLE 22

The method of Examples 19 and 20 may be repeated, with comparable results, replacing sulfuric acid with hydrochloric acid, Dowex 50W or Amberlite GC-120.

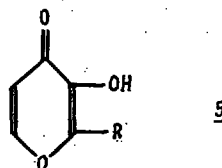
EXAMPLE 23

To a small flask was added 1.58 g (0.01 mol) of intermediate 4 ($R=CH_3$, $R'=CH_3$) and 25 ml of benzene followed by 3.7 ml of boron trifluoride etherate. After stirring for 24 hours at 25°C, the solvent was removed, the residue extracted with chloroform, and the chloroform removed to yield maltol ($R=CH_3$).

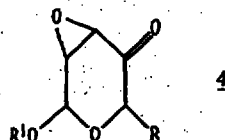
Substantially the same results are obtained when boron trifluoride etherate is replaced with p-toluenesulfonic acid, formic acid, zinc chloride or tin tetrachloride.

WHAT WE CLAIM IS:—

1. A process for preparing a gamma-pyrone of the general formula:—



wherein R is a hydrogen atom, an alkyl group of 1 to 6 carbon atoms, an alkenyl group of 2 to 6 carbon atoms or a phenyl or benzyl group, which comprises reacting a compound of the general formula:—



wherein R is as defined above and R' is an alkyl group of 1 to 6 carbon atoms with an aqueous acid solution.

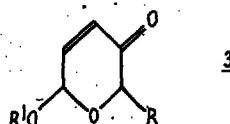
2. A process according to claim 1, wherein the acid solution is derived from sulphuric acid, hydrochloric acid, boron trifluoride etherate, p-toluenesulphonic acid, formic acid, zinc chloride or tin tetrachloride.

3. A process according to claim 1 or 2, wherein the gamma-pyrone of formula 5 is 2-methyl-3-hydroxy gamma-pyrone.

4. A process according to claim 1 or 2, wherein the gamma-pyrone of formula 5 is 2-ethyl-3-hydroxy-gamma-pyrone.

5. A process according to claim 1 or 2, wherein the gamma-pyrone of formula 5 is 2-vinyl-3-hydroxy-gamma-pyrone.

6. A process according to claim 1, wherein the compound of formula 4 is prepared by reacting a compound of the general formula:

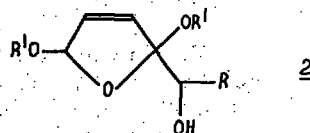




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wherein R and R' are as defined in claim 1, with hydrogen peroxide.

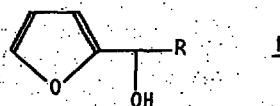
7. A process according to claim 6, wherein the compound of formula 3 is prepared by reacting a compound of the general formula:—



wherein R and R' are as defined in claim 1, with a substantially anhydrous acid.

8. A process according to claim 7, wherein the substantially anhydrous acid is formic acid, trifluoroacetic acid, *p*-toluenesulphonic acid, methanesulphonic acid, citric acid, oxalic acid, chloroacetic acid, sulphuric acid, hydrochloric acid or phosphoric acid.

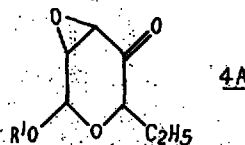
9. A process according to claim 7 or 8, wherein the compound of formula 2 is prepared by reacting a compound of the formula:



wherein R is as defined in claim 1, with an alcoholic (R'OH) solution of chlorine or bromine.

10. A process for preparing gamma-pyrones according to claim 1 and substantially as hereinbefore described with reference to the Examples.

11. A compound of the formula:—



wherein R' is an alkyl group of 1 to 6 carbon atoms.

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