

PATENT SPECIFICATION

(11) 1 538 373

1 538 373

- (21) Application No. 4241/78 (22) Filed 21 July 1977
 (61) Divided out of No. 1538371
 (31) Convention Application No. 710901
 (32) Filed 2 Aug. 1976
 (31) Convention Application No. 721885
 (32) Filed 9 Sept. 1976 in
 (33) United States of America (US)
 (44) Complete Specification published 17 Jan. 1979
 (51) INT CL² C07D 407/12 309/40
 (52) Index at acceptance

C2C 1671 215 220 226 22Y 247 253 25Y 28X 313 314 31Y 337
 351 352 364 36Y 388 500 50Y 624 635 672 760 TZ

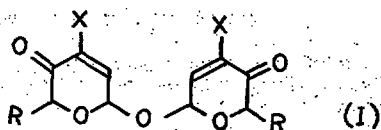


(54) PROCESS FOR THE PREPARATION OF 6,6'-OXY BIS [4-HALO-2H-PYRAN-3(6H)-ONES] AND THEIR USE IN PREPARING GAMMA-PYRONES

(71) We, PFIZER INC., a Corporation organised 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:—

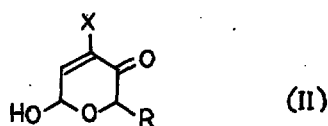
This invention relates to novel 6,6' - oxy bis[4 - halo - 2H - pyran - 3(6H)ones], a process for their production and a process for their further conversion to gamma-pyrone, particularly to maltol (3 - hydroxy - 2-methyl - 4H - pyran - 4 - one) and related compounds.

Thus according to the invention there are provided novel compounds of the general formula:



wherein R is hydrogen, alkyl of 1 to 4 carbon atoms, phenyl or benzyl, and X is chlorine or bromine.

Such dimers are prepared by dehydration of a 4 - halo - dihydropyran of the general formula:

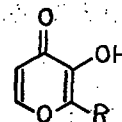


where R and X are as defined above, by heating under vacuum.

4 - Halo - dihydropyrans of formula (II) are described and claimed in our co-pending

application 4242/78 (Serial No. 1,538,374) of even date.

Hydrolysis of the 6,6' - oxybis[4 - halogeno - 2H - pyran - 3(6H) - one] of formula (I) by heating an aqueous solution until hydrolysis is substantially complete yields a gamma-pyrone of the formula:



where R is as previously defined.

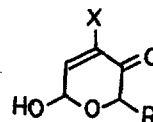
The preparation of the novel compounds of the invention and their conversion to gamma-pyrone is illustrated by the following Examples.

Example 1

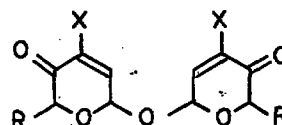
4 - Bromo - 6 - hydroxy - 2 - methyl - 2H-pyran - 3(6H) - one was heated under vacuum for 16 hours at 40°C. The resulting oily solid was crystallized from isopropyl alcohol to yield 6,6' - oxybis[4 - bromo - 2 - methyl-2H - pyran - 3(6H) - one], mp 125°C.

Example 2

The method of Example 1 may be repeated starting with a compound of the formula



to yield a compound of the formula

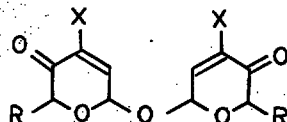


wherein R is hydrogen, ethyl, propyl, butyl, phenyl or benzyl; X is bromine or chlorine.

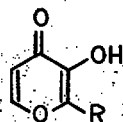
	R	X	M.P. (°C.)
5	CH ₃	Cl	177—179
	CH ₂ CH ₃	Cl	132—135

Example 3

A compound of the formula



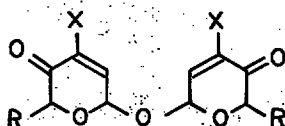
- 10 wherein R is hydrogen, methyl, ethyl, propyl, butyl, phenyl or benzyl and X is bromine or chlorine is refluxed for about 5 hours in 35% phosphoric acid to yield a compound of the formula



- 15 wherein R is as defined above.

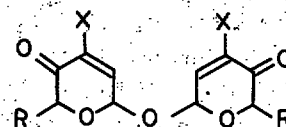
WHAT WE CLAIM IS:—

1. A compound of the general formula

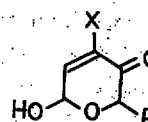


- 20 wherein R is hydrogen, alkyl of 1 to 4 carbon atoms, phenyl or benzyl; and X is chlorine or bromine.

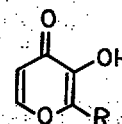
2. A process for preparing a compound of the general formula



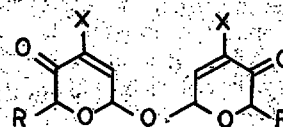
wherein R is hydrogen, alkyl of 1 to 4 carbon atoms, phenyl or benzyl; X is chlorine or bromine which comprises dehydrating under vacuum a compound of the general formula



3. A process for preparing a gamma-pyrone of the general formula



which comprises heating in aqueous solution at 70—160°C until hydrolysis is substantially complete a compound of the formula



wherein R is hydrogen, alkyl of 1 to 4 carbon atoms, phenyl or benzyl; X is chlorine or bromine.

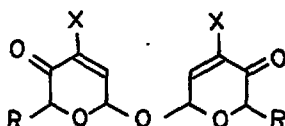
4. A process as claimed in claim 2 or 3 substantially as hereinbefore described with reference to the Examples.

P. C. C. GRAHAM,
Chartered Patent Agent,
Agent for the Applicants.

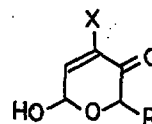
* C L M S *

O=C1C(=C(X)C(=O)O1)R
O=C1C(=C(X)C(=O)O1)F

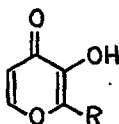
wherein R is hydrogen, alkyl of 1 to 4 carbon atoms, phenyl or benzyl; X is chlorine or bromine which comprises dehydrating under vacuum a compound of the general formula



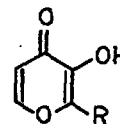
10 wherein R is hydrogen, methyl, ethyl, propyl, butyl, phenyl or benzyl and X is bromine or chlorine is refluxed for about 5 hours in 35% phosphoric acid to yield a compound of the formula



3. A process for preparing a gamma-pyrone of the general formula



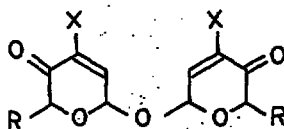
15 wherein R is as defined above.



which comprises heating in aqueous solution at 70–160°C until hydrolysis is substantially complete a compound of the formula

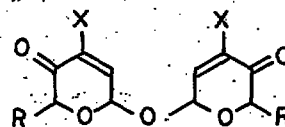
WHAT WE CLAIM IS:—

1. A compound of the general formula



20 wherein R is hydrogen, alkyl of 1 to 4 carbon atoms, phenyl or benzyl; and X is chlorine or bromine.

2. A process for preparing a compound of the general formula



wherein R is hydrogen, alkyl of 1 to 4 carbon atoms, phenyl or benzyl; X is chlorine or bromine.

4. A process as claimed in claim 2 or 3 substantially as hereinbefore described with reference to the Examples.

P. C. C. GRAHAM,
Chartered Patent Agent,
Agent for the Applicants.