

PATENT SPECIFICATION

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NO DRAWINGS

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(54) A PROCESS FOR THE PRODUCTION OF AROMATIC LACTONES

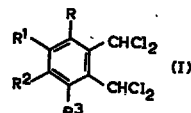
(71) We, **FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT** of 509, Leverkusen, Germany, a corporate body organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of aromatic lactones.

It is already known that benzal chloride(s) can be reacted with concentrated sulphuric acid at elevated temperature to give benzaldehyde(s). This process may be similarly applied to aromatic compounds containing the group $-\text{CHCl}_2$ two or more times in the molecule, in which case the corresponding dialdehydes or polyaldehydes are obtained. When reacted with concentrated sulphuric acid, *ortho*-bis-(dichloromethyl)-benzene also gives the *ortho*-phthalaldehyde by a similar mechanism (see E. Hjelt, *Berichte der Deutschen Chemischen Gesellschaft*, 18 (1885) 2881). In the hitherto known reaction, partial substitution of nuclear hydrogen atoms by chlorine atoms in the aromatic *ortho*-bis-(dichloromethyl)- compounds did not have any effect on the course of the reaction. Thus, trichloro-*o*-bis-(dichloromethyl)-benzene is hydrolysed with concentrated sulphuric acid to give trichloro-*o*-phthalaldehyde (see German Patent No. 360,414, *Frdl.* 14, 378).

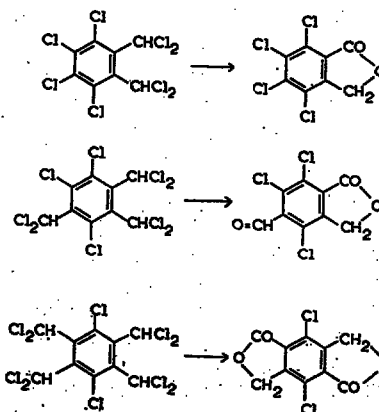
Surprisingly, a process for the production of aromatic lactones has now been found in which aromatic compounds which contain at least two *ortho*-dichloromethyl groups and all of whose hydrogen atoms are substituted by other CHCl_2 groups and/or by chlorine atoms are hydrolysed with at least 75% sulphuric acid or oleum at temperatures in the range of from 80 to 200°C.

The aromatic compounds suitable for reaction in the process according to the invention correspond to the general formula:



in which the radicals R, R¹, R² and R³ which may be the same or different represent chlorine atoms and/or OHCl_2 groups, or R together with R¹ or R¹ together with R² form part of another aromatic ring system which may be substituted by chlorine atoms and/or CHCl_2 groups.

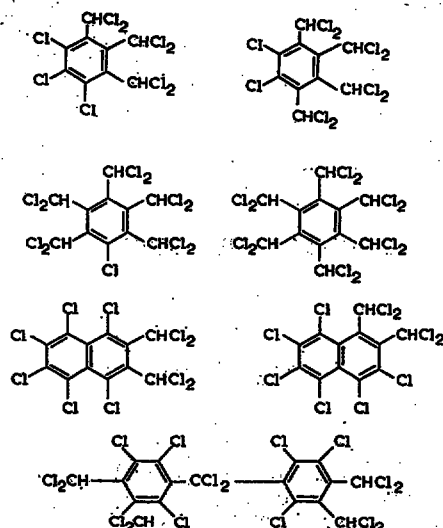
The following examples from the benzene series are intended to illustrate the process according to the invention:



The *ortho*-bis-(dichloromethyl)-compounds used as starting materials are known from the literature or can be obtained by known processes by the nuclear- and/or side-chain chlorination of aromatic compounds substituted by at least two adjacent methyl groups, for which purpose it has proved to be of particular advantage that the *ortho*-bis-(dichloromethyl)-compounds required for the process according to the invention should represent stable terminal chlorination stages which can be obtained in high yields and in a highly

pure form. The compounds listed below represent stable terminal chlorination stages such as these and are mentioned as examples of starting materials for the claimed process:

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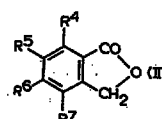


The *ortho*-bis-(dichloromethyl)-compounds are reacted to form the required aromatic lactones by introduction into concentrated sulphuric acid, (at least 75%), or into oleum, preferably with stirring, followed by heating to the required reaction temperature. This temperature varies from one halogen compound to another although it is easily recognised by the appearance of gaseous hydrogen chloride. According to the invention the temperature is in the range from 80 to 200°C. and preferably from 110°C. to 180°C. The cessation in the evolution of HCl signifies the end of the hydrolysis reaction.

The sulphuric acid used to carry out the process according to the invention contains at least 75% by weight of H₂SO₄, although it is of course possible to use 100% sulphuric acid. A commercial grade 96 to 98% sulphuric acid is preferably used. Instead of sulphuric acid, it is also possible to use oleum, a 100% sulphuric acid containing up to 65% and preferably up

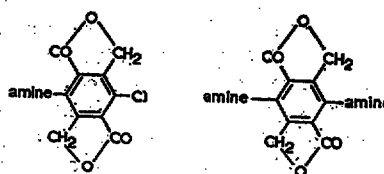
to 20% of SO₃. The quantity in which the sulphuric acid is used is generally such that the reaction mixture can still be effectively stirred. The reaction product is with advantage worked up by stirring the reaction mixture into ice water or crushed ice, the lactones being precipitated in the form of solid substances. They are isolated in the usual way by filtration under suction and washing with water.

The compounds obtainable by the process according to the invention are new, apart from 3,4,5,6-tetrachlorophthalide, and correspond to the general formula:

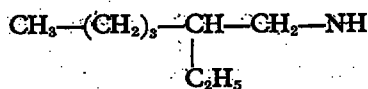


in which the radicals R⁴, R⁵, R⁶ and R⁷ which may be the same or different represent chlorine atoms and/or CHO-groups or alternatively R⁴ together with R⁵ or R⁶ together with R⁷ form part of another aromatic ring which may be substituted by chlorine atoms and/or CHO groups, in which case two adjacent radicals form a lactone ring with the group —CH₂—O—CO.

The aromatic lactones produced by the process according to the invention represent valuable intermediate products. They may be reacted *inter alia* with primary or secondary amines with one or more chlorine atoms being exchanged, to form fluorescent dyes or optical brighteners. Some properties of compounds such as these are listed in the following Table. The fluorescent dye indicated appears on exposure to ultra-violet light:



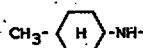
Amine:



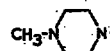
Properties:

Yellowish crystals, m.p. 105°C.
blue fluorescence

Amine:



Amine:



Properties:

Yellow crystals, m.p. 330°C.
yellowish/green fluorescence

Amine:

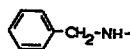


Properties:

Yellowish crystals, m.p. 219°C.
blue fluorescence

Amine:

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**Properties:**

Yellowish crystals, m.p. 230°C.
blue fluorescence

Properties:

Yellow crystals, m.p. 348°C.
yellowish/green fluorescence

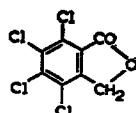
Amine:**Properties:**

Yellow crystals, m.p. 331°C.
yellowish/green fluorescence

- 10 The process according to the invention is illustrated by the following Examples in which percentages specified are percentages by weight.

EXAMPLE 1

- 15 381 g (1 mol) of tetrachloro-1,2-bis-(dichloromethyl)-benzene were introduced at room temperature into 1900 ml of concentrated sulphuric acid (98% by weight). The reaction mixture was heated with vigorous stirring to 110—120°C. over a period of 10 hours, during which a stream of nitrogen was passed through it. After cooling, the clear, dark red reaction solution was poured onto ice and the tetrachlorophthalide precipitated was washed neutral with water. After drying, the 25 3,4,5,6-tetrachlorophthalide which corresponds to the formula:

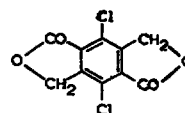


was recrystallised from benzene to yield bright yellow needles melting at 207 to 208°C.

- 30 Yield: 225 g (82% of the theoretical).
The mixed melting point with an authentic preparation (see C. Graebe, A. 238, 330 (1887)) did not show any depression. The IR- and NMR-spectra of both samples were identical.

EXAMPLE 2

- 360 g (0.75 mol) of α H, α' -H, α'' -H, α''' -H-decachlorodureol were introduced into 1000 ml of concentrated sulphuric acid (98% by weight). The mixture was heated to 170—190°C. until the evolution of HCl stopped (after about 10 hours). After cooling, the reaction mixture was stirred into 3 kg of crushed ice, and the precipitate was suction-filtered and washed thoroughly with water. 3,6-Dichloropyromellitide was thoroughly boiled with 750 ml of acetone, suction-filtered and dried *in vacuo* at 100°C. An almost colourless powder corresponding to the formula:



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m.p. above 365°C.

Yield: 168 g=86.7% of the theoretical.

$C_{10}H_2Cl_4O_2$ (MW 259)

Calculated: C 46.33 H 1.54 Cl 27.41 O 24.71

Found : C 46.31 H 1.72 Cl 27.15 O 24.38

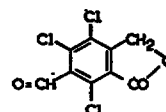
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The infra-red spectrum of this compound shows a carbonyl band at 1760 cm^{-1} which corresponds to the lactone structure.

EXAMPLE 3

215 g (0.5 mol) of trichloro-1,2,4-tris-(dichloromethyl)-benzene were introduced with vigorous stirring into 1000 ml of concentrated sulphuric acid (98% by weight). The reaction mixture was heated to 120—130°C. over a period of 10 hours during which nitrogen was passed through it. After cooling, the reaction mixture was poured onto ice. The 3,5,6-trichloro-4-formylphthalide which corresponds to the formula:

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was washed neutral with water and dried at 100°C. in a vacuum drying cabinet: ochre-coloured powder melting at 140°C.

Yield: 102 g (77% of the theoretical).

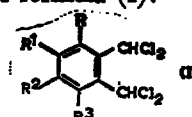
The infra-red spectrum of this compound shows two carbonyl bands, one at 1770 cm^{-1} with corresponds to the lactone group, and the other at 1705 cm^{-1} which corresponds to the aldehyde group.

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WHAT WE CLAIM IS:—

1. A process for the production of an aromatic lactone, wherein an aromatic compound of the general formula (I):

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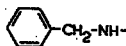


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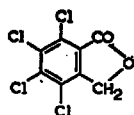
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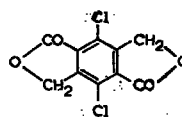
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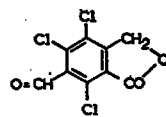
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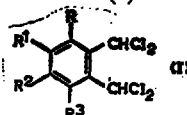
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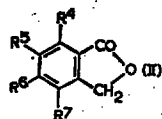


wherein the radicals R, R¹, R² and R³, which may be the same or different, represent chlorine atoms and/or CHCl₂-groups or R together with R¹ or R¹ together with R² form part of another aromatic ring system which may be substituted by chlorine atoms and/or CHCl₂ groups is hydrolysed with at least 75% by weight sulphuric acid or oleum at a temperature of from 80°C to 200°C.

2. A process as claimed in claim 1, wherein the hydrolysing is carried out at a temperature of from 110°C to 180°C.

3. A process as claimed in claim 1 or 2, wherein the sulphuric acid is 96% to 98% by weight sulphuric acid.

4. Aromatic lactones corresponding to the general formula:



in which the radicals R⁴, R⁵, R⁶ and R⁷ which

may be the same or different represent chlorine atoms and/or CHO groups or R⁴ together with R⁵ or R⁵ together with R⁶ form part of another aromatic ring which may be substituted by chlorine atoms and/or CHO groups, in which case two adjacent radicals form a lactone ring with the group —CH₂—O—CO, excluding the case where each of R⁴, R⁵, R⁶ and R⁷ are chlorine atoms.

5. A process as claimed in claim 1 substantially as herein described with reference to any of the specific Examples.

6. Aromatic lactones when prepared by a process as claimed in any of claims 1 to 3 and 5.

7. Aromatic lactones as claimed in claim 4 as herein described with reference to any of the specific Examples.

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