

FORM 2
The Patent Act 1970,
(39 of 1970)
&
The Patent rule 2003
Complete Specification
(See Section 10 and Rule 13)

1. TITLE OF THE INVENTION

"An improved process for manufacture of 4-chloro-4'-hydroxy benzophenone"

2. APPLICANT(S)

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3. PREAMBLE OF THE DESCRIPTION

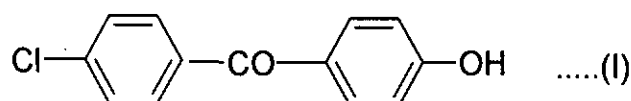
The following specification particularly describes the invention and the manner in which it is to be performed.

Field of Invention

The present invention relates to the method of manufacture of 4-Chloro,4'-Hydroxy Benzophenone (4-CHBP) (I) . This is an important precursor to the preparation of poly(arylene ether ketones).In further details , the present invention relates to the method of manufacture of 4-Chloro,4'-Hydroxy Benzophenone, using a one pot synthesis route as well as cheap raw materials. In further details the present invention relates to simple methods of purifying the Crude 4-Chloro,4'-Hydroxy Benzophenone, to a sufficient purity that it can be used for polymerization purposes.

Background of the Invention

It is known to make 4-Chloro,4'-Hydroxy Benzophenone(I) by the Fries rearrangement



of phenyl p-chlorobenzoate in the presence of $AlCl_3$ without solvent. This is described in the article written by VP Malik & GS Saharia in Journal of Scientific and Industrial Research Vol.15B, pp 633-635 ,November 1956. It is also known from GB 1,574,441 to prepare (I) by the reaction of p-chlorobenzoic acid and phenol in the presence of a molar excess of liquid anhydrous HF. European Patent 75,390 and Japanese Patent 03127753 describe the manufacture of (I) by the reaction of p-chlorobenzoic acid and phenol in the presence of Trifluoromethane sulphonic acid. More recently the Japanese Patent 03041047 has disclosed a method of making (I) by the reaction of p-hydroxy benzoyl chloride and excess Chlorobenzene in the presence of $AlCl_3$, to give pure (I) in 51% yield. Pure (I) is prepared by acetylating the crude (I) with acetic anhydride and crystallizing the acetylated (I) and then hydrolyzing in refluxing NaOH solution.

The above methods of preparation of (I), suffer from a number of disadvantages which make it unattractive for an industrial process. The first method via Fries rearrangement requires the isolation of the ester and its subsequent rearrangement. The second method, involving the single step reaction of p-Chlorobenzoic acid and phenol uses the very expensive and corrosive acylating agents like Trifluoromethane sulphonic acid and HF. Moreover with HF, there is a necessity to use pressure equipment . And also the purification methods are cumbersome.

Object of the Invention

Hence it is desired to overcome the disadvantages of the past methods of preparation of (I) by developing a process using a single step procedure using cheaply available raw materials and further purifying the crude product (I) by simple methods to >99.5% purity, sufficient for polymerization purposes.

Description of the Invention

It has been found by the method of this invention described below, that 4-Chloro, 4'-hydroxy benzophenone (I), can be prepared in excellent yield by reacting p-chlorobenzoyl chloride with phenol and a suitable Lewis acid in suitable solvent. The reaction proceeds via the Phenyl ester of the acid chloride. However to a certain extent the reaction also proceeds via direct (i.e. one stage) nuclear acylation. This method can be operated in a conventional industrial plant as a "one-pot" process. Moreover relatively cheaper starting materials are used. Also the yield of 4-CHBP is 85% as >95% pure. Additionally a method of purification of the product is disclosed which is relatively easy and uses readily available solvents to produce (I) of sufficient purity for polymerization to the desired poly(arylene ether ketones).

The process of the invention may be conveniently effected at a temperature in the range from 30°C up to 120°C. The reaction may be carried out in an inert solvent. Suitable inert solvents include Nitrobenzene and o-dichlorobenzene. The temperature of the reaction used is dependant on the solvent. For example, using Nitrobenzene, a temperature range of 60°C-110°C is preferred and more particularly a temperature range of 80°C-100°C is even more preferred. Using o-dichlorobenzene, a temperature range of 50°C-100°C is preferred and more particularly a temperature range of 70°C-90°C is even more preferred. The time of reaction is dependant on the temperature of the reaction and for example varies from 40 hours at 50°C to 6 hours at 100°C.

For the process of this invention it is preferred to use a slight excess of the acid chloride to the phenol, for example from 1.01 to 1.20 moles of the acid chloride for each mole of the Phenol. It is particularly more preferred to use an excess of from 1.05-1.10 moles of acid chloride for each mole of phenol.

The Lewis acid used is preferably Aluminum Chloride. The amount of Aluminum Chloride used in the process of the invention is in an amount of at least one mole and preferably from 1.05 to 2.5 moles/mole. It is found that increased use of Aluminum Chloride increases the yield and Purity as well as shortens the reaction time. Hence the process of the invention has been particularly found to be effective when the Aluminum Chloride used is between 1.5 to 2.1 moles per mole.

While carrying out the process of this invention it is also observed that the evolution of HCl is continuous throughout the reaction and commences with the addition of Phenol to Aluminum Chloride slurry in the solvent.

In a preferred process according to this invention, phenol is added to a mixture of Aluminum Chloride in o-DCB. Subsequently PCBC is added slowly to the reaction mixture while maintaining the reaction mixture at a particular temperature. When all the PCBC has been added, the temperature is raised to the appropriate level and the reaction continued. After workup the desired product is obtained in high yield (80-85%) and in high purity (95-99%) with very little of the isomeric impurity, 4-Chloro, 2'-hydroxy Benzophenone. However the product thus obtained is not suitable for polymerization and must be further purified.

A simple method of purification is also described in the process of this invention by which process material of sufficient purity is obtained suitable for polymerization purposes. The impurities present in the crude material may be separated by crystallization from suitable solvents. Suitable solvents according to the process of this invention are mixtures of aromatic hydrocarbon solvents like Benzene, Toluene and Xylene and polar solvents like Acetone, methanol and ethanol. According to the method of this invention, the amount of the polar solvent is just such as to dissolve the crude 4-Chloro, 4'-hydroxy benzophenone in the aromatic hydrocarbon under refluxing conditions. Subsequently the polar solvent is distilled off and the solution allowed to cool to 15°-25°C. The 4-Chloro, 4'-hydroxy benzophenone is filtered as crystalline material of purity >99.5% and 72% overall yield.

The invention is illustrated but not limited by the following examples.

Example 1

In a 1 Lit Round bottom flask is charged 300 ml o-dichlorobenzene followed by 273.7 gm $AlCl_3$. 103.4 gm Phenol dissolved in 100 ml o-dichlorobenzene is charged over 2 hours. The RM is stirred for one hour at 30-35°C. To this is added 175 gm p-chlorobenzoyl chloride in 100 ml o-dichlorobenzene over 2 hours at 30-35°C. Reaction is exothermic and cooling is to be applied. The reaction mass is heated to 90°C and maintained at this temperature for 12 hours. The reaction mass is drowned in 0.5N HCl. The solids that are precipitated are filtered and washed with water. The cake is purified by dissolving in sodium hydroxide solution, filtration and acidification to give crude Crop 1, I = 198 gm, 85% yield with p-CHBP purity >95%. The cake is further purified to make it suitable for polymerization by crystallization and charcoal treatment from Toluene and acetone to get 99.9% HPLC purity, M.Pt of 180-181°C and 72% overall yield.

Example 2

In a 1 Lit Round bottom flask is charged 300 ml Nitrobenzene followed by 200 gm $AlCl_3$. 103.4 gms Phenol dissolved in 100 ml Nitrobenzene is charged over 2 hours. The RM is stirred for one hour at 30-35°C. To this is added 175 gm p-chlorobenzoyl chloride in 100 ml Nitrobenzene over 2 hours at 30-35°C. Reaction is exothermic and cooling is to be applied. The reaction mass is heated to 90°C and maintained at this temperature for 8 hours. The reaction mass is drowned in 0.5N HCl. The solids that are precipitated are filtered and washed with water. The cake is purified by dissolving in

sodium hydroxide solution, filtration and acidification to give crude Crop 1, I = 186 gm, 80% yield with p-CHBP purity >95%. The cake is further purified to make it suitable for polymerization by crystallization from Toluene and acetone to get 99.9% HPLC purity, M.Pt of 180-181°C and 66% overall yield.

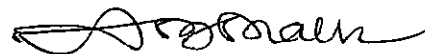
Example 3

In a 1 Lit Round bottom flask is charged 300 ml o-dichlorobenzene followed by 200 gm $AlCl_3$. 103.4 gm Phenol dissolved in 100 ml ODCB is charged over 2 hours. The RM is stirred for one hour at 30-35°C. To this is added 175 gm p-chlorobenzoyl chloride in 100 ml o-dichlorobenzene over 2 hours at 30-35°C. Reaction is exothermic and cooling is to be applied. The reaction mass is heated to 80°C and maintained at this temperature for 12 hours. The reaction mass is drowned in 0.5N HCl. The solids that are precipitated are filtered and washed with water. The cake is purified by dissolving in NaOH solution, filtration and acidification to give crude Crop 1, I = 181 gm, 78% yield with p-CHBP purity >95%. The cake is further purified to make it suitable for polymerization by crystallization from toluene and acetone to get 99.9% HPLC purity, M.Pt of 180-181°C and 65% overall yield.

Claims We claim,

1. A process for the preparation of 4-Chloro, 4'-hydroxy benzophenone which comprises a one step reaction between p-chlorobenzoyl chloride and phenol in the presence of a lewis acid in a solvent.
2. A process as claimed in claim 1 where the reaction is carried out in the temperature range of 30-120°C.
3. A process as claimed in claim 1 where the solvent is Nitrobenzene or o-dichlorobenzene
4. A process as claimed in Claim 1 where the Lewis acid used is Aluminum Chloride
5. A process as claimed in Claim 1 where the Amount of Aluminium Chloride used is in the range 1.05 to 2.5
6. A process as claimed in any one of Claims 1 to 5 where a mixture of Phenol and inert solvent is treated first with Aluminum Chloride and then subsequently with p-chlorobenzoyl chloride or vice versa.
7. A process for further purifying the 4-Chloro, 4'-hydroxy benzophenone produced by the process as claimed in Claim 1 to 7 by solvent crystallization using a mixture of an aromatic hydrocarbon and a polar solvent .
8. A process as claimed in Claim 7 wherein the the aromatic hydrocarbon is any one of Benzene, Toluene or Xylene and the polar solvent is any one of acetone, methanol or ethanol.

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Dated 13 December 2005

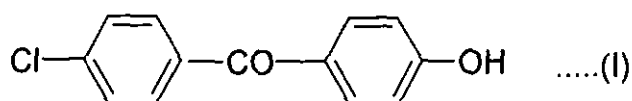


Applicants

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Abstract

4-Chloro,4'-Hydroxy Benzophenone (I)



was prepared in 71-72% total yield and >99.5% purity. A one pot synthesis of I by acylation of phenol with 4-Chloro,4'-Hydroxy Benzophenone in the presence of AlCl_3 and workup of the reaction mass to give Crude (I) in >95% purity and Yield of 85%. Crude (I) was further purified to give >99.5% pure (I). Thus to Phenol dissolved in ODCB is added AlCl_3 . To this is added 4-Chloro,4'-Hydroxy Benzophenone, and the whole mass maintained at 80°C for 12 hours. The reaction mass is worked up by drowning in dilute HCl solution and Crude(I) of purity >95% ppts. out. This is further purified by to give >99.5% pure material in 71-72% yield