(CONVENTION. By one or more persons and/or a Comp 4

COMMONWEALTH OF A

Patents Act 1952-196

CONVENTION APPLICATION FOR A PATENT

601191

FEE STAMP TO VALUE OF $..150.. ATTACHED
MAIL OFFICER.....

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address (es).

Ixx/We (1) BASF AKTIENGESELLSCHAFT

of D-6700 Ludwigshafen, Federal Republic of Germany

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)

ACYLATION OF AROMATICS

(3) Here insert number(s) of basic application(s)

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered (3)

P36 19 169.8 and P36 42 329.7

(4) Here insert Name of basic Country or Countries, and basic date or dates

for a patent or similar protection made in (4) Federal Republic of Germany on 6th June 1986 and 11th December 1986

APPLICATION ACCEPTED AND AMENDMENTS ALLOWED 26-6-90

My/Our address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys, 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 4th day of June 19 87

(5) Signature (s) of Applicant (s) or Seal of Company and Signatures of its Officers as prescribed by its Articles of Association.

(5) BASF AKTIENGESELLSCHAFT

by Louis C. Gebhardt

Registered Patent Attorney

LODGED AT SUB-OFFICE
- 5 JUN 1987
Melbourne

To:

THE COMMISSIONER OF PATENTS.

(CONVENTION. Company.) Form 8

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1962

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

(1) Here insert (in full) Name of Company.

In support of the Convention Application made by(1) BASF Aktiengesellschaft, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany (hereinafter referred to as the applicant) for a Patent for an invention entitled:(2) "ACYLATION OF AROMATICS"

(2) Here insert title of Invention.

(3) Here insert full Name and Address, of Company official authorized to make declaration.

We, ~~I~~(3) HELMUT MATTHIAS and PETER BARZ, citizens of the Federal Republic of Germany, residing, respectively, of at 2 Fruehlingstrasse, 6730 Neustadt; and 20 Hochfeldstrasse, 6700 Ludwigshafen; Federal Republic of Germany do solemnly and sincerely declare as follows:

1. ~~I~~ We are authorised by the applicant for the patent to make this declaration on its behalf.

2. The basic applications as defined by Section 141 of the Act ~~was~~ were made in(4) the Federal Republic of Germany under No. P 36 19 169.8 on the 6th day of June 1986, by BASF Aktiengesellschaft,

(4) Here insert basic Country or Countries followed by date or dates and basic Applicant or Applicants.

on the 11th day of December 1986, by BASF Aktiengesellschaft

(5) Here insert (in full) Name and Address of Actual Inventor or Inventors.

3.(5) MANFRED EGGERSDORFER, HARDO SIEGEL, ALFRED SCHUHMACHER and ~~and~~ JOCHEM HENKELMANN, WALTER GROSCH, citizens of the Federal Republic of Germany, residing, respectively, at 18 Hannongstrasse, 6710 Frankenthal, 25 Hans-Purrmann-Allee, 6720 Speyer; 36 Von-Weber-Strasse, 6700 Ludwigshafen; and 1 Starenweg, 6803 Edingen-Neckarhausen; Fed.Rep.of Federal Republic of Germany; 44 Ludwigshafener Strasse, 6704 Mutterstadt, Germany; ~~is~~/are the actual inventor of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant is the assignee of MANFRED EGGERSDORFER, HARDO SIEGEL, ALFRED SCHUHMACHER and WALTER GROSCH and JOCHEM HENKELMANN

4. The basic applications referred to in paragraph 2 of this Declaration ~~was~~ were the first applications made in a Convention country in respect of the invention the subject of the application.

DECLARED at 6700 Ludwigshafen, Federal Republic of Germany, this 22nd day of May 19 87.

(6) Signature.

(6) BASF Aktiengesellschaft

ppa. Matthias ppa. Barz

To: THE COMMISSIONER OF PATENTS.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-73893/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 601191

(54) Title
ACYLATION OF AROMATICS BY FRIEDEL-CRAFTS REACTION

International Patent Classification(s)
(51)[4] **C07C 045/46** **C07C 049/76** **C07C 065/34** **C07C 051/373**

(21) Application No. : **73893/87** (22) Application Date : **05.06.87**

(30) Priority Data

(31) Number	(32) Date	(33) Country
3619169	06.06.86	DE FEDERAL REPUBLIC OF GERMANY
3642329	11.12.86	DE FEDERAL REPUBLIC OF GERMANY

(43) Publication Date : **10.12.87**

(44) Publication Date of Accepted Application : **06.09.90**

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(74) Attorney or Agent
WATERMARK MELBOURNE

(56) Prior Art Documents
DE 1288584
AU 53205/79 C07C 45/15, C07D 307/46, 333/22

(57) Claim

1. A process for the acylation of an aromatic by the Friedel-Crafts method, wherein the acylation is carried out in the presence of a metalalkyl or metalalkyl halide of beryllium, magnesium, boron, gallium, indium, thallium, silicon, tin, lead, antimony, zinc, cadmium, mercury, titanium and/or aluminium.

2. A process as claimed in claim 1, wherein a acyl halide or carboxylic anhydride is reacted with an alkylaromatic to give an alkyl-substituted aromatic ketone.

3. A process as claimed in claim 1 or claim 2, wherein a metalalkyl or metalalkyl halide of aluminium, magnesium, boron, tin, zinc or titanium is used.

4. A process as claimed in claim 1 or claim 2, wherein a trialkylaluminum halide of the formula Ia

.../2

$$R_nALX_{3-n} \qquad \text{Ia}$$

where the radicals R are identical or different alkyl groups of 1 to 12 carbon atoms, X is halogen and n is 1, 2 or 3, or a mixture of two compounds of the formula I is used.

COMMONWEALTH OF AUSTRALIA 601191 Form 10

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

Class Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority :

Related Art :

This document contains the amendments made under Section 49 and is correct for printing.

Name of Applicant : BASF AKTIENGESELLSCHAFT

Address of Applicant : D-6700 Ludwigshafen, Federal Republic of Germany

Actual Inventor: MANFRED EGGERSDORFER, HARDO SIEGEL, ALFRED SCHUHMACHER, WALTER GROSCH and JOCHEM HENKELMANN

Address for Service : EDWD. WATERS & SONS,
50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

ACYLATION OF AROMATICS

The following statement is a full description of this invention, including the best method of performing it known to :- us

Acylation of aromatics

The present invention relates to an improved process for the acylation of aromatics by the Friedel-Crafts method, in particular for the preparation of alkyl-substituted aromatic ketones by reacting a carbonyl halide or carboxylic anhydride with an alkylaromatic in the presence of a Friedel-Crafts catalyst.

The Friedel-Crafts acylation of aromatics, ie. the introduction of an acyl group into aromatic compounds by the action of an acylating agent on aromatics in the presence of certain metal halides, for example aluminum chloride, is generally known, for example from Houben-Weyl, Methoden der org. Chem., vol. VII/2a, 1973, pages 15-39 and 311-325. The disadvantage of this process is the occurrence of side reactions, in particular when alkyl-substituted aromatics are acylated. For example, resinous byproducts are formed, the alkyl group is eliminated and isomerization occurs, especially when aromatics having secondary or tertiary alkyl radicals are reacted. According to various publications, these side reactions are supposed to be due to an interaction of $AlCl_3$ and hydrogen chloride, which, if not present in the catalyst, is formed during the Friedel-Crafts acylation (cf. C.A. Olah, Friedel-Crafts and Related Reactions, vol. I, page 207 and vol. III, Part I, page 550 et seq., Interscience 1964). In order to suppress the side reactions, it is recommended that freshly sublimed catalysts be used and the resulting hydrogen halide be removed from the reaction mixture by using reduced pressure or passing through an inert gas (cf. C.A. Olah, Friedel-Crafts and Related Reactions, vol. III, page 549, and literature cited there). Although the isomerization can to a certain extent be suppressed by these measures, as also disclosed in German Published Application DAS 2,720,294, the result is still unsatisfactory; further separation of the resulting product mixtures is complicated and in many cases cannot be carried out economically, so that the corresponding mixtures have to

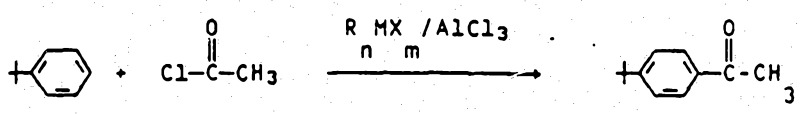
be used for subsequent reactions. Another disadvantage is that substantial amounts of the reactants are removed from the reaction mixture, resulting in poor yields.

It is an object of the present invention to improve the Friedel-Crafts acylation of aromatics in such a way that side reactions are substantially avoided and the products are obtained in high yields. In particular, it is intended to suppress the elimination and isomerization of the alkyl groups in the conversion of alkylaromatics.

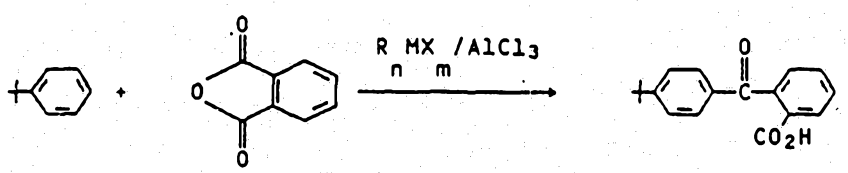
We have found that this object is achieved by a process for the acylation of aromatics by the Friedel-Crafts method, wherein the acylation is carried out in the presence of a metalalkyl or metalalkyl halide of metals or semimetals of main groups two to five and/or metals of subgroups two or four of the Periodic Table.

The novel process can be particularly advantageously used for reacting carbonyl halides or carboxylic anhydrides with alkylaromatics to give alkyl-substituted ketones. Where a) acetyl chloride or b) phthalic anhydride and tert-butylbenzene are used as starting materials and a mixture of a metalalkyl or metalalkyl halide and aluminum chloride is used as the catalyst, the reaction can be represented by the following equations:

a)



b)



where R is alkyl, X is halogen, M is a metal or semimetal, n is from 1 to 4, m is from 0 to 4 and m + n is the valency of the metal.

According to the invention, the Friedel-Crafts acylation is carried out in the presence of effective amounts of metalalkyls or metalalkyl halides of metals or semimetals of main groups two to five, in particular three, of the Periodic Table and metals of subgroups two and/or four. They may be represented by the general formula

$$R_nMX_m \qquad I$$

where the radicals R are identical or different alkyl groups of 1 to 12, preferably 1 to 6, in particular 1 to 4, carbon atoms, eg. methyl, ethyl, n-propyl, isopropyl, n-butyl or isobutyl, M is a metal or semimetal of the stated groups, eg. beryllium, magnesium, boron, gallium, indium, thallium, silicon, tin, lead, antimony, zinc, cadmium, mercury or titanium, X is fluorine, chlorine, bromine or iodine, for cost reasons chlorine frequently being preferred, n is from 1 to 4 and m is from 0 to 4, and the sum of n and m is the valency of the metal.

Mixtures of different compounds I can also be used.

The preparation of the organometallic compounds I can be carried out in a conventional manner, for example as described in Brockhaus ABC Chemie, 2 (1971), 867-869.

Particularly suitable compounds for the novel process are organometallic compounds of magnesium, such as dialkylmagnesium or Grignard compounds (RMgX), of boron, such as trialkylboron, dialkylboron halide or alkylboron dihalide, of tin, such as tetraalkyltin or trialkyltin halides, or of titanium, such as alkyltitanium trihalide or dialkyltitanium dihalide, and organozinc and organocadmium compounds, such as dialkylzinc or dialkylcadmium. Organozinc compounds are particularly preferably used. Aluminumalkyls and alkylaluminum halides, for example those of the formula Ia

$$R_nAlX_{3-n} \qquad Ia$$

where the radicals R are identical or different alkyl groups of 1 to 12, preferably 1 to 6, in particular 1 to 4, carbon atoms, eg. methyl, ethyl, n-propyl, isopropyl, n-butyl or isobutyl, X is fluorine, chlorine, bromine or

iodine, for cost reasons chlorine being preferred, and n is 1, 2 or 3, or mixtures of two different compounds of the formula Ia are particularly preferred.

The following compounds are listed as examples: methylmagnesium chloride, ethylmagnesium bromide, diethylmagnesium, trimethylboron, triethylboron, diethylboron chloride, diethylboron bromide, ethylboron dichloride, tetramethyltin, tetraethyltin chloride, methyltitanium trichloride, diethyltitanium dichloride, dimethylcadmium and in particular dimethylzinc, diethylzinc, dipropylzinc, dibutylzinc and ethylzinc chloride.

Particularly preferred compounds are methylaluminum dichloride and dibromide, ethylaluminum dichloride and dibromide, isopropylaluminum dibromide, n-hexylaluminum dichloride, dodecylaluminum diiodide, dimethylaluminum chloride, diethylaluminum bromide and dibutylaluminum iodide. Mixtures of these compounds are, for example, methylaluminum sesquichloride, ethylaluminum sesquichloride or mixtures of an alkylaluminum dichloride and a dialkylaluminum chloride in a molar ratio of, for example, from 20:1 to 1:20.

Instead of the alkylaluminum halides, trialkylaluminum, eg. trimethyl-, triethyl-, tri-n-propyl-, triisopropyl-, tri-n-butyl- or tri-n-hexylaluminum, or aluminumalkyls having mixed alkyl radicals, eg. methyldiethylaluminum, can also advantageously be added to the reaction mixture.

Suitable Friedel-Crafts catalysts are the conventional compounds, such as $FeCl_3$, BF_3, $ZnCl_2$ or $TiCl_4$. Aluminum halides, preferably aluminum bromide and in particular aluminum chloride, are particularly suitable.

Suitable aromatics are the compounds conventionally used for Friedel-Crafts reactions, such as isocyclic and heterocyclic aromatic hydrocarbons. In the novel process, alkylaromatics, eg. alkyl-substituted benzenes, naphthalenes, anthracenes, furans, benzofurans, thiophenes etc., can particularly advantageously be reacted.

Alkyl radicals are, for example, those of 1 to 20, in particular 1 to 12, preferably 1 to 8, carbon atoms. The alkyl radical and the aromatic nucleus may carry further substituents, such as halogen, eg. chlorine or bromine, C_1-C_4-alkyl, C_1-C_4-alkoxy or hydroxyl; the alkyl radical may furthermore contain double or triple bonds. Alkylbenzenes having one or two branched or straight-chain alkyl radicals are preferably reacted. Examples of alkylbenzenes are:

toluene, ethylbenzene, n-propylbenzene, isopropylbenzene, n-butylbenzene, sec-butylbenzene, tert-butylbenzene, n-pentylbenzene (2-methylbutyl)-benzene, (3-methylbutyl)-benzene, (1-methylbutyl)-benzene, (1,1-dimethylpropyl)-benzene, n-hexylbenzene, (1-ethyl-1-methylpropyl)-benzene, (1,1-dimethylbutyl)-benzene, (1-methylpentyl)-benzene, (1-ethyl-1-methyl)-benzene, (1-ethylhexyl)-benzene, oct-4-ylbenzene, 1,2-dimethylbenzene and 1,4-diethylbenzene.

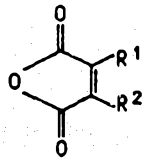
The acylating agents used are the conventional compounds, in particular carbonyl halides and carboxylic anhydrides, as well as imide chlorides and the carboxylic acids themselves.

There are no restrictions with regard to the carbonyl halides or carboxylic anhydrides to be converted; for example, the acyl fluorides, iodides and in particular bromides and chlorides can be reacted. As a rule, the acyl chlorides of aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic carboxylic acids are reacted. Acyl chlorides of the formula R^1COCl, where R^1 is hydrogen or an aliphatic radical, eg. alkyl of 1 to 20, in particular 1 to 8, carbon atoms, unsubstituted or substituted aryl, preferably phenyl, which, where substituted, may carry in particular 1 or 2 substituents such as C_1-C_4-alkyl, aryloxy, such as phenoxy, halogen, such as fluorine, chlorine or bromine, or nitro, may be listed as examples. R^1 may furthermore be aralkyl, such as benzyl, or a heterocyclic radical, preferably an oxygen-containing or sulfur-containing heterocyclic radical having 5 or 6

ring members, eg. furanyl, pyranyl or a thiophene radical.

Examples of acyl chlorides are the following: formyl chloride, acetyl chloride, propionyl chloride, n-butyryl chloride, n-octadecanoyl chloride, 3,3-dimethylacryloyl chloride, benzoyl chloride, 3-methoxybenzoyl chloride, 3-phenoxybenzoyl chloride, o-chlorobenzoyl chloride, 3-chloro-5-methylbenzoyl chloride, 2,6-dichlorobenzoyl chloride, m-bromobenzoyl chloride, o-bromobenzoyl chloride, p-methylbenzoyl chloride, p-tert-butylbenzoyl chloride, p-nitrobenzoyl chloride, p-carbomethoxybenzoyl chloride, m-carbobutoxybenzoyl chloride, phenylacetyl chloride, 4-chlorophenylacetyl chloride, cinnamyl chloride, 4-chlorocinnamyl chloride, furan-2-carbonyl chloride and thiophene-2-carbonyl chloride.

Suitable anhydrides are those of aliphatic, cycloaliphatic, araliphatic, aromatic or heterocyclic mono- or dicarboxylic acids. Anhydrides of monocarboxylic acids are, for example, those of alkylcarboxylic acids, such as acetic anhydride, propionic anhydride, n-butyric anhydride or benzoic anhydride. Anhydrides of dicarboxylic acids are, for example, those of the formula



where R^2 has the same meanings as R^1 and furthermore R^1 and R^2 can be bonded to one another to form an unsubstituted or substituted aromatic ring system, for example a benzene ring. Examples are maleic anhydride, succinic anhydride, methylmaleic anhydride, tetraethylsuccinic anhydride, phthalic anhydride and 4,5-methylenedioxyphthalic anhydride.

Advantageously, stoichiometric amounts of the aromatic compound and the acylating agent can be used. However, it is also possible to use one of the two components in an excess compared with the other component; for example, from 1 to 1.5 moles of the aromatic can be

used per mole of acylating agent.

The amounts of catalyst usually employed for Friedel-Crafts reactions may also be used in the novel process, the total amount of catalyst corresponding to the sum of the Lewis acid, such as aluminum halide, and the organometallic compound I.

The addition of the organometallic compound results in binding of the hydrogen chloride present or formed in the reaction mixture. The effective amount therefore depends on the number of alkyl radicals present in the molecule. The ratio of the isomerization products (for example, in the case of tert-amyl-substituted aromatics, the tertiary/secondary alkyl ratio) and the amount of by-products can be influenced by the amount of metalalkyl or metalkyl halide. As a rule, from 0.1 to about 1.1 equivalents of metalalkyl, in the form of the metalalkyl or metalalkyl halide, and from 0.1 to 1.5 moles of a Friedel-Crafts catalyst, e.g., an aluminum halide, can be added per equivalent of carbonyl halide, it being advantageous to use a small excess, e.g., a 10% excess, of the Friedel-Crafts catalyst. Larger excess amounts can be used but are of no advantage. In the case of carboxylic anhydrides or carbonyl halides which carry substituents which form stable complexes with Friedel-Crafts catalysts, e.g., aluminum halides and organometallic compounds, one equivalent of catalyst is additionally required per substituent.

In the preferred embodiment of the process a mixture of the Friedel-Crafts catalyst and the trialkylaluminum or alkylaluminum halide is used in an amount of from 1 to 1.5, preferably of from 1.1 to 1.2 moles per equivalent of acyl halide or in an amount of from 2 to 2.5 moles per equivalent of acyl halide. If starting materials containing substituents which form stable complexes with the catalyst are used, the total amount of catalyst must be increased correspondingly. The effective amount of the organoaluminum compound is advantageously from 0.1 to about 1 mole of alkylaluminum dihalide, about 0.05-0.5 mole of dialkylaluminum halide or about 0.03-0.33 mole

used per mole of acylating agent.

The amounts of catalyst usually employed for Friedel-Crafts reactions may also be used in the novel process, the total amount of catalyst corresponding to the sum of the Lewis acid, such as aluminum halide, and the organometallic compound I.

The addition of the organometallic compound results in binding of the hydrogen chloride present or formed in the reaction mixture. The effective amount therefore depends on the number of alkyl radicals present in the molecule. The ratio of the isomerization products (for example, in the case of tert-amyl-substituted aromatics, the tertiary/secondary alkyl ratio) and the amount of by-products can be influenced by the amount of metalalkyl or metalkyl halide. As a rule, from 0.1 to about 1.1 equivalents of metalalkyl, in the form of the metalalkyl or metalalkyl halide, and from 0.1 to 1.5 moles of a Friedel-Crafts catalyst, e.g., an aluminum halide, can be added per equivalent of carbonyl halide, it being advantageous to use a small excess, e.g., a 10% excess, of the Friedel-Crafts catalyst. Larger excess amounts can be used but are of no advantage. In the case of carboxylic anhydrides or carbonyl halides which carry substituents which form stable complexes with Friedel-Crafts catalysts, e.g., aluminum halides and organometallic compounds, one equivalent of catalyst is additionally required per substituent.

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of trialkylaluminum, in each case per equivalent of carboxylic acid derivative, such as acyl halide or anhydride. Larger amounts up to complete replacement of the aluminum halide are possible, but for economic reasons the amount of organoaluminum compound is kept as small as possible.

The reaction can be carried out in the absence or, advantageously, in the presence of a solvent, suitable solvents being the conventional solvents for Friedel-Crafts reactions, for example chlorobenzene, dichlorobenzene, 1,2-dichloroethane, carbon disulfide, nitromethane or nitrobenzene. The amount of solvent is not critical; in general, from 200 to 1000 g of solvent can be used per mole of alkylbenzene.

The reaction can be carried out in a conventional manner, and the starting materials can be reacted at from -20 to 100°C, preferably from 0 to 60°C, in particular from 10 to 40°C, under superatmospheric, reduced or, preferably, atmospheric pressure.

Advantageously, the carbonyl halide or carboxylic anhydride is initially taken together with the solvent, and the aluminum halide is added, followed by the alkylaromatic mixed with the metalalkyl or metalalkyl halide.

Working up of the reaction mixture and isolation of the products are carried out in a conventional manner, for example by pouring the reaction mixture onto water and/or ice, separating off the aqueous phase and isolating the ketone by distillation or crystallization.

Surprisingly, the aromatic ketones, which are useful intermediates and end products, for example for dyes, auxiliaries, crop protection agents and drugs, can be prepared by the novel process in yields which are higher than those obtained in the prior art. Furthermore, it is possible to acylate alkyl-substituted, in particular tert-alkyl-substituted, aromatics without pronounced isomerization of the alkyl radical; this is particularly important in the synthesis of (tert-amylbenzoyl)-benzoic acid, since

the latter is an important intermediate for the preparation of tert-amylanthraquinone, which is required for the production of hydrogen peroxide (cf. German Laid-Open Application DOS 2,013,299).

EXAMPLE 1

Preparation of 4-tert-butylacetophenone

78 g (1 mole) of acetyl chloride in 100 ml of dichlorobenzene were initially taken, and 73 g (0.6 mole) of $AlCl_3$ were then added a little at a time. A mixture of 134 g (1 mole) of tert-butylbenzene and 60 g (0.5 mole) of diethylaluminum chloride in 50 ml of 1,2-dichlorobenzene was added dropwise to this solution at from 15 to 20°C in the course of 5 hours. The mixture was then stirred for a further hour at 30°C.

When the reaction was complete, the reacted mixture was poured onto a mixture of 1 l of H_2O with 300 g of ice and 30 ml of concentrated H_2SO_4, and the organic phase was separated off, dried and distilled.

Yield: 162 g (92% of theory) of 4-tert-butylacetophenone.

EXAMPLE 2

Preparation of 4-tert-amylpropiophenone

The following were reacted as described in Example 1:

92 g (1 mole) of propionyl chloride,
148 g (1 mole) of tert-amylbenzene,
27 g (0.2 mole) of $AlCl_3$ and
113 g (0.9 mole) of ethylaluminum dichloride.

Yield: 184 g (90% of theory) of 4-tert-amylpropiophenone.

EXAMPLE 3

Preparation of 2-(4'-tert-amylbenzoyl)-benzoic acid

The following were reacted in 300 ml of dichlorobenzene, as described in Example 1:

74 g (0.5 mole) of phthalic anhydride
74 g (0.5 mole) of tert-amylbenzene,
73 g (0.6 mole) of $AlCl_3$ and
63 g (0.5 mole) of ethylaluminum dichloride.

Yield: 133 g (90% of theory) of 2-(4'-tert-amylbenzoyl)-benzoic acid.

COMPARATIVE EXAMPLES 3a AND 3b

The reaction was carried out as described in Example 3, but in the presence of

a) 145 g (1.1 moles) of $AlCl_3$ in 150 ml of dichlorobenzene, without the addition of ethylaluminum dichloride, and

b) as described in Example a) but while passing in dry air during the reaction.

When the reaction was complete, the reacted mixture was poured onto a mixture of 1 l of water with 300 g of ice and 30 ml of concentrated H_2SO_4, the organic phase was extracted with dilute sodium hydroxide solution, and the amylbenzoylbenzoic acids were precipitated from the aqueous phase with sulfuric acid and dried to give a) 120.5 g and b) 115 g of a solid which, according to HPLC analysis, had the following composition (percentages by area in HPLC):

	a)	b)
2-(4-tert-amylbenzoyl)-benzoic acid	52%	71%
2-(4-sec-amylbenzoyl)-benzoic acid	43%	24%
benzoylbenzoic acid	2%	2%
others	3%	3%

EXAMPLE 4

Preparation of 2-(4'-tert-amylbenzoyl)-benzoic acid

The following were reacted in 300 ml of dichlorobenzene, as described in Example 1:

74 g (0.5 mole) of phthalic anhydride,
74 g (0.5 mole) of tert-amylbenzene,
81.3 g (0.6 mole) of $AlCl_3$ and
51.4 g (0.25 mole) of methylaluminum sesquichloride, $(CH_3)_3Al_2Cl_3$.

Yield: 139 g (94% of theory) of 2-(4'-tert-amyl-benzoyl)-benzoic acid.

EXAMPLE 5

Preparation of 2-[4'-(1-ethyl-1-methylpentylbenzoyl)]-benzoic acid

The following were reacted as described in Example 1:

74 g (0.5 mole) of phthalic anhydride,
95 g (0.5 mole) of (1-ethyl-1-methylpentyl)-benzene,
113 g (0.85 mole) of $AlCl_3$ and
30 g (0.25 mole) of diethylaluminum chloride.

Yield: 154 g (91% of theory) of 2-[4'-ethyl-1-methylpentylbenzoyl)]-benzoic acid.

EXAMPLE 6

Preparation of 2-(4'-tert-amylbenzoyl)-benzoic acid

The following were reacted as described in Example 3:

74 g (0.5 mole) of phthalic anhydride,
74 g (0.5 mole) of tert-amylbenzene,
97 g (0.8 mole) of $AlCl_3$ and
34 g (0.3 mole) of triethylaluminum.

Yield: 127 g (86% of theory) of 2-(4'-tert-amyl-benzoyl)-benzoic acid.

EXAMPLE 7

74 g (0.5 mole) of phthalic anhydride in 200 ml of o-dichlorobenzene were initially taken, and 128 g (1.05 moles) of $AlCl_3$ were added a little at a time at from 15 to 20°C. A mixture of 8.3 g (0.07 mole) of diethylzinc and 74 g (0.5 mole) of tert-amylbenzene was added dropwise to the reaction solution in the course of 5 hours at this temperature. The mixture was then stirred for a further 2 hours at room temperature.

When the reaction was complete, the reacted mixture was poured onto a mixture of 1 l of water with 300 g of ice and 30 ml of concentrated H_2SO_4, the organic phase was extracted with dilute sodium hydroxide solution, and the amylbenzoylbenzoic acids were precipitated from the

aqueous phase with sulfuric acid and dried. 133 g (90% of theory) of a mixture of 2-(4'-tert-amylbenzoyl)-benzoic acid and 2-(4'-sec-isoamylbenzoyl)-benzoic acid (tertiary/secondary ratio = 79:21) were obtained.

EXAMPLE 8

74 g (0.5 mole) of phthalic anhydride were reacted with 128 g (1.05 moles) of $AlCl_3$ and 25 g (0.2 mole) of diethylzinc in 74 g of tert-amylbenzene, similarly to Example 1. After the mixture had been worked up, 118 g (80% of theory) of pure 2-(4'-tert-amylbenzoyl)-benzoic acid were obtained.

EXAMPLE 9

74 g (0.5 mole) of phthalic anhydride and 134 g (1.10 moles) of $AlCl_3$ were reacted with 20 g (0.2 mole) of triethylboron in 74 g of tert-amylbenzene for 8 hours, as described in Example 1. After the mixture had been worked up in a conventional manner, 127 g (86% of theory) of a mixture of 2-(4'-tert-amylbenzoyl)-benzoic acid and 2-(4'-sec-isoamylbenzoyl)-benzoic acid (tertiary/secondary ratio = 60:40) were obtained.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the acylation of an aromatic by the Friedel-Crafts method, wherein the acylation is carried out in the presence of a metalalkyl or metalalkyl halide of beryllium, magnesium, boron, gallium, indium, thallium, silicon, tin, lead, antimony, zinc, cadmium, mercury, titanium and/or aluminium.

2. A process as claimed in claim 1, wherein a acyl halide or carboxylic anhydride is reacted with an alkylaromatic to give an alkyl-substituted aromatic ketone.

3. A process as claimed in claim 1 or claim 2, wherein a metalalkyl or metalalkyl halide of aluminium, magnesium, boron, tin, zinc or titanium is used.

4. A process as claimed in claim 1 or claim 2, wherein a trialkylaluminum halide of the formula Ia

$$R_nALX_{3-n} \qquad \text{Ia}$$

where the radicals R are identical or different alkyl groups of 1 to 12 carbon atoms, X is halogen and n is 1, 2 or 3, or a mixture of two compounds of the formula I is used.

5. A process as claimed in claim 1 or 2 or 3 or 4, wherein the metalalkyl halide used is a metalalkyl chloride or bromide.

6. A process as claimed in claim 1 or 2 or 3 or 4 or 5, wherein the Friedel-Crafts catalyst used is aluminum chloride or bromide.

7. A process as claimed in claim 1 or 2 or 3 or 4 or 5 or 6, wherein the aromatic used is an alkylbenzene.

8. A process as claimed in claim 2 or 3 or 4 or 5 or 6 or 7, wherein a mixture of the Friedel-Crafts catalyst and the trialkylaluminum or alkylaluminum halide is used in an amount of from 1 to 1.5 moles per equivalent of acyl halide or in an amount of from 2 to 2.5 moles per equivalent of anhydride.

9. A process as claimed in claim 2 or 3 or 4 or 5 or 6 or 7, wherein from 0.1 to 1 mole of alkylaluminum dihalide or from 0.03 to 0.33 mole of trialkylaluminum is used per equivalent of acyl halide anhydride.

DATED this 27th day of November, 1989.

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