PATENT SPECIFICATION

(11) 1 580 967

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(21) Application No. 15287/77 (22) Filed 13 April 1977
(31) Convention Application No. 2616382
(32) Filed 14 April 1976
(31) Convention Application No. 2616588
(32) Filed 14 April 1976 in
(33) Federal Republic of Germany (DE)
(44) Complete Specification published 10 Dec. 1980
(51) INT CL^3 C07C 43/30
(52) Index at acceptance
C2C 200 220 226 227 22Y 30Y 351 355 364 36Y 388 500 50Y 625
634 652 665 699 FE UR

(54) MANUFACTURE OF MONOACETALS OF AROMATIC 1,2-DIKETONES

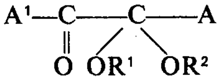
(71) We, BASF AKTIENGESELLSHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention relates to a process for the manufacture of monoacetal of an aromatic 1,2-diketone from the corresponding 1,2-diketone.

The polymerization of unsaturated monomers, or of their mixtures with unsaturated polymers, by UV irradiation in the presence of photoinitiators has been disclosed. Though many photoinitiators are already known, their practical usefulness is restricted by some inherent disadvantages. For this reason, new compounds suitable for this application are of particular interest. The more recently discovered photoinitiators include compounds of the type of benzil-monoacetals (cf. U.S. Patent 3,715,293, German Laid-Open Applications DOS 2,232,365 and 2,337,813), which do not suffer from some of the disadvantages of earlier photoinitiators. The conventional process for the manufacture of compounds of this type is described by Kuhn and Trieschmann in Chemische Berichte *94* (1961), 2258 and in German Laid-Open Application DOS 2,337,813; according to this process, compounds of the benzil type are reacted with a dialkyl sulfite in the presence of an acid and an alcohol to give the corresponding monoacetals.

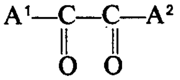
The present invention seeks to provide a further process for the manufacture of monoacetals of aromatic 1,2-diketones from the corresponding 1,2-diketones, which may provide an improved simple production of the monoacetals, in high yields and under economically advantageous conditions, and which furthermore may permit the production of non-cyclic unsymmetrical monoacetals of the stated type.

The present invention provides a process for the manufacture of a monoacetal of an aromatic 1,2-diketone of the formula (I)



$$A^1{-}\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}{-}\!\!{-}\underset{OR^1\ \ OR^2}{C}{-}\!\!{-}A^2 \qquad \text{(I)}$$

where A^1 and A^2 are identical or different aromatic radicals which may or may not be substituted and R^1 and R^2 are identical or different hydrocarbon radicals of 1 to 12 carbon atoms which may or may not be substituted, from a corresponding aromatic 1,2-diketone of the formula (II)



$$A^1{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}A^2 \qquad \text{(II)}$$

wherein the 1,2-diketone of the formula (II) is reacted, in an organic solvent, with an alkylating agent $(R^1)_nX$ and an alcoholate $(R^2O)_mMe$, where R^1 and R^2 have the above meanings, n and m are integers from 1 to 3, X is a monobasic, dibasic or tribasic acid radical and Me is a non-transition metal of group 1, 2 or 3 of the periodic table of the elements, preferably a metal of atomic number from 11 to 20.

Suitable aromatic diketones of the formula (II) are especially those where A^1 and A^2 are an unsubstituted or substituted benzene radical, suitable substituents being, above all, hydrocarbon radicals of 1 to 10 carbon atoms, e.g. alkyl or phenyl, alkoxyalkyl radicals of 2 to 10 carbon atoms, alkoxy radicals of 1 to 10 carbon atoms or halogen.

Examples of particularly suitable aromatic 1,2-diketones which may be used for a process within the invention are benzil and substituted benzils, e.g. 4,4' - dimethylbenzil, 4,4' - diisopropylbenzil, 4,4' - diphenylbenzil, 2,2' - dimethoxybenzil, 4,4' - dimethoxybenzil, 4 - methylbenzil, 3 - methoxybenzil, 2,2' - dimethylbenzil, 4 - chloro - 4' - phenylbenzil, 4,4' - dichlorobenzil, 3,3' - dibromobenzil, 2,4,2',4' - tetramethylbenzil, 2,4,6 - trimethylbenzil and 2,4 - dichloro - 4' - methylbenzil. The manufacture of these benzil derivatives is described in the literature; for example, they may be manufactured by oxidizing the corresponding benzoins.

Alkylating agents suitable for the process have the above formula $(R^1)_nX$ and are esters of monobasic, dibasic or tribasic acids, especially of acids containing a sulfur, phosphorus or halogen atom. Examples are the esters of sulfuric acid, of sulfurous acid, of phosphoric acid and of phosphorous acid, R^1 halides e.g. the chlorides, bromides and iodides (which can be considered to be esters of the hydrohalic acids), and the esters of aliphatic and aromatic sulfonic acids, such as the mesylates, tosylates, brosylates and benzenesulfonates. The sulfates, halides and sulfonic acid esters are particularly suitable, and amongst these the sulfates are preferred. The radical R^1 is a substituted or unsubstituted hydrocarbon radical of 1 to 12 carbon atoms, examples being, above all, the appropriate alkyl (especially of 1 to 6 carbon atoms), aralkyl (especially of 7 to 9 carbon atoms), alkenyl (especially of 3 to 5 carbon atoms) and aralkenyl (especially of 9 or 11 carbon atoms) radicals, and the groups $Z—(CHR^3—CHR^4)_p—$ or $Z—(CHR^3)_p—$, where p is a number from 1 to 3, R^3 and R^4 are H or CH_3 and Z is halogen or OR^5, SR^5, OAr or SAr, where R^5 is alkyl of 1 to 4 carbon atoms or alkoxyalkyl of 1 to 5 carbon atoms and Ar is a six-membered aromatic radical.

Examples of alkylating agents which can be used for this process are dimethyl sulfate, diethyl sulfate, dihexyl sulfate, diallyl sulfate, dicrotyl sulfate, di-(β-phenylethyl) sulfate, di-(γ-phenylallyl) sulfate, di-(2 - methoxyethyl) sulfate, di - (2 - phenoxyethyl) sulfate, di - (methylthioethyl) sulfate and di - (2 - phenylthioethyl) sulfate.

Most of the suitable alkylating agents are known to those skilled in the art and are commercially available as such, sometimes being referred to as agents for basic or cold alkylation, or are simple to manufacture in accordance with processes disclosed in the literature.

Alcoholates used for the manufacture of symmetrical acetals are the alcoholates corresponding to the alkylating agent ($R^1=R^2$), i.e. for example, a methylate, e.g. sodium methylate or potassium methylate, when using dimethyl sulfate, or, for example, sodium ethylate when using ethyl bromide.

To manufacture the unsymmetrical acetals, alcoholates which do not correspond to the alkylating agent ($R^1\neq R^2$) are used, i.e., for example, an ethylate, e.g. sodium ethylate or potassium ethylate, when using dimethyl sulfate, or, for example, sodium ethylate when using allyl bromide. In other respects, the above data regarding the radicals R^1 apply, in a general sense, to the nature of the radicals R^2. Sodium and potassium alcoholates are preferred.

Examples of organic solvents (which include solvent mixtures) which are very suitable for the present process are aromatic solvents, e.g. benzene, toluene, xylene or o-dichlorobenzene and aliphatic solvents, e.g. dioxane, tetrahydrofuran, glycol ethers, ethylene chloride or dimethylformamide. Dioxane is a preferred solvent; for the manufacture of symmetrical acetals, dimethylformamide is also a preferred solvent. The amount of solvent should advantageously be such that after mixing all the reactants the reaction mixture can still be stirred easily. This is generally the case if the solvent accounts for at least about half the reaction mixture.

The reaction, according to the invention, of the 1,2 - diketone with the alkylating agent and the alcoholate is in general carried out at from −50° to +150°C, preferably at from −20° to 100°C. The reaction time depends on the particular reactants, the temperature and the batch size. In general, however, the reaction is complete within a few hours and in some cases it is complete almost as soon as the reactants have been brought together.

Theoretically, 1/n mole of alkylating agent of the above formula $(R^1)_nX$ is reacted with 1 mole of 1,2-diketone and 1/m mole of alcoholate of the above formula $(R^2O)_mMe$, with n and m in the fractions corresponding to the numbers n and m, respectively, in the formulae of the alkylating agent and alcoholate used, in order to produce the symmetrical or unsymmetrical monoacetals of the aromatic 1,2-diketones. In general it is however preferred to use some of the reactants in excess in order to achieve complete conversion. Thus, from 1/n to 10/n mole or more, preferably from 1/n to 4/n mole, of alkylating agent, and from 1/m to 10/m mole or more, preferably from 1/m to 4/m mole, of alcoholate can be used per mole of 1,2-diketone.

In an advantageous embodiment of the present invention, the process is carried out by introducing the alcoholate into a reaction mixture consisting of the aromatic 1,2-diketone, the alkylating agent and the solvent. The alcoholate can, in such cases, be added as the solid or as a slurry, for example in dimethylformamide, dioxane or tetrahydrofuran. A further possible way of adding the alcoholate is in the form of a very concentrated solution in the alcohol on which the alcoholate is based. An example is a solution of about 20% by weight strength of sodium methylate in methanol. However, the process can also be carried out by adding the alkylating agent as the last component to the reaction mixture.

In a further embodiment of the present invention, the reactants are brought together in any sequence in a non-polar solvent, e.g. toluene, preferably at room temperature, and the mixture is stirred. The reaction to give the 1,2-diketone monoacetal can be accelerated by gradually adding a polar solvent, e.g. dimethylformamide or dioxane.

After the reaction has ended (which can very easily be ascertained by, for example, thin layer chromatography), it is advisable to destroy any residual dimethyl sulfate by adding bases, e.g. ethanolamine or aqueous sodium hydroxide solution, with or without heating of the reaction solution. During the process and the isolation of the reaction products, it is necessary to ensure that the reaction mixture does not assume an acid pH, otherwise hydrolysis of the monoacetal to the corresponding 1,2-diketone may occur.

The reaction mixture can be worked up, and the reaction product isolated, by conventional processes, e.g. precipitation, extraction or distillation. An example of a suitable procedure is simply to add water to the reaction solution, or run the reaction solution into water. Hereupon, the desired monoacetals of the 1,2-diketones frequently separate out as a crystalline precipitate or, in some cases, as oils. A precondition for this method is, however, that the solvent used for the reaction is water-miscible.

A particularly preferred method of working up the reaction solution is to remove the solvent from the reaction mixture, after addition of water, by azeotropic distillation. After this distillation the water-insoluble monoacetal separates out, especially on cooling, as a crystalline substance or as an oil, often in an analytically pure or virtually analytically pure form. This method offers the advantage that the solvent employed in the reaction can be substantially recovered.

The acetals obtained are outstandingly suitable for use as photoinitiators, especially for the photopolymerization of olefinically unsaturated monomers, and of mixtures of such monomers, by means of UV radiation. Reference is directed in this connection to our UK patent specification No. 1,431,224 and our compending GB patent application No. 15288/77, (Serial No. 1580968). The photoinitiators are very suitable for photocuring coatings based on unsaturated polyester resins, and for the imagewise photocrosslinking of photosensitive materials for photoresists or photopolymer printing plates. Especially when using the unsymmetrical acetals, layers of photo-crosslinkable systems can be cured rapidly, to give coatings having a scratch-resistant surface and exhibiting very little yellowing.

In the Examples which follow, parts and percentages are by weight. Parts by volume bear the same relation to parts as that of the liter to the kilogram.

EXAMPLE 1

78 parts of sodium methylate are added in portions in the course of 6 hours to a solution of 210 parts of benzil and 177 parts of dimethyl sulfate in 800 parts by volume of dioxane at room temperature, whilst stirring. A solution of 56 parts of sodium hydroxide in 1,000 parts by volume of water is then added to the reaction mixture and the batch is heated for about 1 hour under reflux. 1,100 parts by

volume of solvent are then distilled off; virtually all the dioxane employed is recovered thereby.

The reaction mixture is then allowed to settle out at slightly above 70°C. The lower aqueous phase is separated off and discarded and the upper organic phase is stirred into 1,000 parts by volume of water. The precipitate is filtered off, washed with water and dried under reduced pressure at 40°C. Without employing any further purification, 246 parts (96% of theory) of analytically pure benzil dimethylacetal of melting point 61—62°C are obtained.

EXAMPLE 2

6 parts of sodium methylate are added in portions in the course of 2 hours to a solution of 21 parts of benzil and 37 parts of p-toluenesulfonic acid methyl ester in 50 parts of dimethylformamide at room temperature, whilst stirring. The reaction mixture is then heated with 500 parts of water for 1 hour under reflux and subsequently cooled to room temperature, and the precipitate is filtered off and recrystallized from a mixture of isopropanol and water. 22 parts of benzil dimethylketal are obtained.

EXAMPLE 3

21.6 parts of sodium methylate are added in portions in the course of 3 hours to a solution of 52.5 parts of benzil and 68.4 parts of benzyl bromide in 400 parts by volume of dimethylformamide at room temperature, whilst stirring. The reaction mixture is then stirred for 30 minutes at room temperature, after which it is stirred into 2,000 parts by volume of water. The precipitate which separates out is filtered off, washed with water and dried. It is then suspended in 150 parts by volume of petroleum ether, filtered off, washed once with petroleum ether and dried. 62.0 parts of benzil methyl-benzyl-monoacetal of melting point 83—84°C are obtained.

EXAMPLE 4

34 parts of sodium ethylate are added in portions, in the course of one hour, to a solution of 52.5 parts of benzil and 63 parts of dimethyl sulfate in 250 parts by volume of dioxane at room temperature, whilst stirring. After adding 300 parts by volume of water and 22 parts of solid sodium hydroxide, the reaction mixture is heated under reflux for 30 minutes, 350 parts by volume of dioxane/water azeotrope are then distilled from the reaction mixture, and the residue, after cooling to room temperature, is extracted with 150 parts by volume of chloroform. 2 parts of animal charcoal are added to the chloroform extract, the extract is boiled up and filtered and the solvent is evaporated off on a rotary evaporator. The oily, substantially colorless residue becomes crystalline after some time. Melting point: 52—54°C.

EXAMPLE 5

48 parts of sodium methylate are added in portions, in the course of 2.5 hours, to a solution of 105 parts of benzil and 121 parts of allyl bromide in 500 parts by volume of dimethylformamide at room temperature, whilst stirring. After adding 2,000 parts by volume of water, the reaction mixture is extracted with four times 100 parts by volume of chloroform and the combined chloroform extracts are then washed with three times 200 parts by volume of water. The chloroform phase is concentrated on a rotary evaporator and the residue is then distilled under reduced pressure. 114 parts of benzil methyl-allylacetal, boiling at 135—136°C/0.3 mm Hg. are obtained.

EXAMPLE 6

Benzil methyl-crotyl-monoacetal, of boiling point 140—145°C/0.3 mm Hg, is prepared by the method described in Example 5. Yield: 119 parts (80% of theory).

EXAMPLE 7

An unsaturated polyester is prepared by esterifying 431 parts of maleic anhydride and 325 parts of phthalic anhydride with 525 parts of 1,2-propylene glycol. After adding 0.01% of hydroquinone, a 66% strength solution of the polyester in styrene is prepared (solution A).

3 parts of photoinitiator are added to 97 parts of solution A (giving solution B). The shelf life (gel time) of this mixture is determined at 60°C, in the absence of light. For the photo-curing experiments, 10 parts of a 1% strength solution of

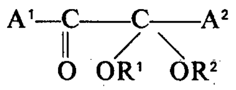
paraffin (softening range 50—52°C) in styrene are added to 100 parts of solution B and the resin is applied, by means of a film spreader (500 μm gap width) onto hard fiberboard coated with photographic paper. After being allowed to evaporate in air for about 2 minutes, the films are exposed to fluorescent lamps (emitting a high proportion of UV light), placed at a distance of 4 cm. The rate of curing is determined by measuring the König pendulum hardness (DIN 53,157) and is summarized in Table 1 together with the color measurements obtained on the cured films.

TABLE 1

Photoinitiator	Pendulum hardness after minutes 4	8	10	Color measurement of the films: yellow index after exposure	Shelf life at 60°C (hours)
benzil methylbenzyl-monoacetal	90	104	108	18.5	78
benzil methylallyl-monoacetal	62	92	99	13.8	56—71
benzil methylcrotyl-monoacetal	74	98	104	11.6	not measured
benzil dimethylmonoacetal	92	105	108	22.1	80—105

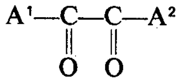
WHAT WE CLAIM IS:—

1. A process for the manufacture of a monoacetal of an aromatic 1,2-diketone, of the formula (I)



$$A^1-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{OR^1\quad OR^2}{C}-A^2 \qquad (I)$$

where A^1 and A^2 are identical or different aromatic radicals which may or may not be substituted and R^1 and R^2 are identical or different hydrocarbon radicals, of 1 to 12 carbon atoms which may or may not be substituted, from a corresponding aromatic 1,2-diketone of the formula (II)



$$A^1-\underset{\underset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle O}{\|}}{C}-A^2 \qquad (II)$$

where the 1,2-diketone of the formula (II) is reacted in an organic solvent with an alkylating agent

$$(R^1)_nX$$

and an alcoholate

$$(R^2O)_mMe$$

wherein R^1 and R^2 have the above meanings, n and m are integers from 1 to 3, X is a monobasic, dibasic or tribasic acid radical and Me is a non-transition metal of group 1, 2 or 3 of the periodic table of the elements.

2. A process as claimed in claim 1, wherein R^1 and R^2 are different radicals of the stated type.

3. A process as claimed in claim 1, wherein R^1 and R^2 are identical, unsubstituted hydrocarbon radicals.

4. A process as claimed in any of claims 1 to 3, wherein an alkylating agent $(R^1)_nX$, where X is the acid radical of sulfuric acid or of a sulfonic acid, or is halogen, is used.

5. A process as claimed in any of claims 1 to 4, wherein dioxane is used as the solvent.

6. A process as claimed in any of claims 1 to 5, wherein in the formula of the aromatic diketone A^1 and A^2 are benzene rings optionally substituted by identical or different substituents selected from alkyl of 1 to 10 carbon atoms, phenyl, alkoxyalkyl of up to 10 carbon atoms, alkoxy of 1 to 10 carbon atoms or halogen.

7. A process as claimed in any of claims 1 to 6, wherein R^1 in the formula of the

alkylating agent is alkyl of 1 to 6 carbon atoms, aralkyl of 7 to 9 carbon atoms, alkenyl of 3 to 5 carbon atoms, aralkenyl of 9 or 11 carbon atoms or Z—(CHR^3—CHR^4)$_p$— or Z—(CHR^3)$_p$— where p is a number from 1 to 3, R^3 and R^4 are hydrogen or methyl and Z is halogen, OR^5, SR^5, OAr or SAr, R^5 being alkyl of 1 to 4 carbon atoms, or alkoxyalkyl of up to 5 carbon atoms and Ar being phenyl.

8. A process as claimed in any of claims 1 to 7 wherein the alcoholate is introduced into a reaction mixture consisting of the aromatic diketone, the alkylating agent and the solvent.

9. A process for the manufacture of a monoacetal of an aromatic 1,2-diketone carried out substantially as described in any of the foregoing Examples.

10. Monoacetals of aromatic 1,2-diketones when manufactured by a process as claimed in any of claims 1 to 9.

11. Use of a non-cyclic unsymmetrical monoacetal of an aromatic 1,2-diketone which has been manufactured by a process as claimed in claim 2, as a photoinitiator for a radiation-curable mixture.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1980
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.