

### Process for preparing quinoline-5,8-diones

The present invention relates to a process for preparing quinoline-5,8-diones which find an application as intermediate products, especially in the pharmaceutical industry.

Bracher (Heterocycles, 29, 2093, 1989) has already mentioned a process for preparing quinoline-5,8-dione from 5-amino-8-hydroxyquinoline by oxidation with dichromate. This process requires a double functionalization of the quinoline nucleus, and thus involves starting materials that are expensive and not readily available. S. Ghosh (J. Fluorine Chem., 1994; 67: 53-56) describes quinoline-5,8-dione derivatives obtained by cycloaddition between p-benzoquinone and a substituted diene. 4-Chloroquinoline-5,8-dione is described as a synthetic intermediate of more complex tricyclic or tetracyclic compounds (M. Croisy-Delsey et al., J. Heterocyclic Chem. 1993; 30: 55-60), whereas 2-methoxyquinoline-5,8-dione is presented as a by-product of the N-alkylation of 2,5,8(1H)-quinoline-trione (C. Avendano et al. Synthesis 1991; 727-730). 4-Hydroxy-5,8-quinolinequinone may be synthesized from 2,5-dimethoxyaniline and from the ester of methylacrylic acid (P. Withopf et al. Tetrahedron, 1987; 43(20):4549-4554). Quinoline-5,8-dione and 2-chloro-4-methylquinoline-5,8-dione are starting materials used in the synthesis of azaanthraquinone derivatives (K.T. Potts et al., J. Org. Chem., 1986:2011-2021). Antimalaria agents derived from 6-amino-5,8-dimethoxyquinolines are prepared from 2-trifluoro-4-methyl or from 2,4-dimethyl quinoline-5,8-dione (C. Temple et al., J. Med. Chem., 1974; 17(6):615-619). Finally, EP 0 433 679 describes quinoline-5,8-dione derivatives as inhibitors of the Maillard reaction in the body, this reaction being responsible (by denaturing proteins via sugars) for

- 2 -

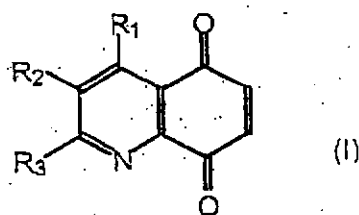
several consequences of diabetes (neuropathy, retinopathy, etc.).

Methods also exist for preparing quinones by photo-oxidation of phenols (for example Chem. Comm., 2173, 1996), but it has never been envisaged to apply such methods to heterocyclic compounds and in particular to quinoline derivatives.

The reason for this is that it was not obvious that such methods would not be hampered by the presence of the electron-withdrawing pyridine nucleus. Reactions between the quinones and the nitrogen of the pyridine nucleus, leading to colored polymers, could also have been feared. This is what was observed with 5-hydroxy-isoquinoline.

It has now been found that a particular group of 8-hydroxyquinolines gives, by photo-oxidation, in the presence of a sensitizer and decomposition of the intermediate hydroperoxide, quinoline-5,8-diones in high yields.

One subject of the present invention is a process for preparing quinoline-5,8-diones of formula:

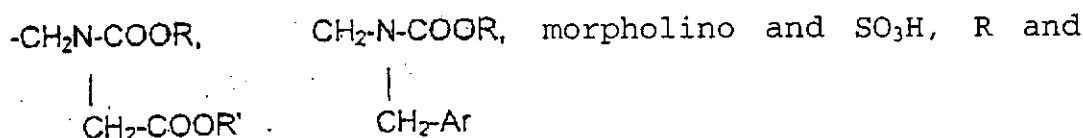


in which:

30

$R_1$ ,  $R_2$  and  $R_3$  are chosen from hydrogen, a halogen atom, a  $C_1$ - $C_6$  alkyl group,  $-CHO$ ,  $-OH$ ,  $-OR$ ,  $-COOH$ ,  $-CN$ ,  $-CO_2R$ ,  $-CONHR$ ,  $-CONRR'$ ,  $-NH_2$ ,  $-NHCOR$ ,

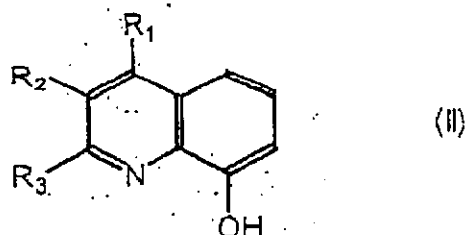
- 3 -



R' being chosen from C<sub>1</sub>-C<sub>6</sub> alkyl groups and Ar being a C<sub>6</sub>-C<sub>14</sub> aryl group,

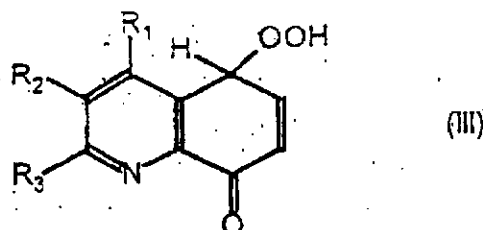
in which an 8-hydroxyquinoline of formula:

5



in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> have the meaning given above, is oxidized with oxygen under the action of actinic radiation in solution in an organic solvent and in the presence of a catalytic amount of a sensitizer, and the hydroperoxide formed, of formula:

10



15

is then decomposed to a compound of formula I.

The oxidation reaction with oxygen is carried out in an organic solvent in which the starting 8-hydroxyquinoline of formula II is soluble. The solvent is advantageously chosen such that the sensitizer is also soluble therein.

20

The sensitizer may especially be tetraphenylporphine (or TPP), in which case the solvent may especially be dichloromethane.

25

- 4 -

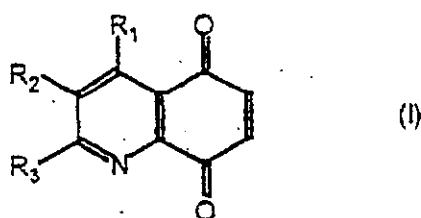
Other suitable sensitizers and solvents may also be used, and in particular:

- rose bengal in  $\text{CH}_3\text{CN}$ ,  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{CHCl}_3$  or water;
- 5 - methylene blue in  $\text{CH}_3\text{CN}$ ,  $\text{MeOH}$ ,  $\text{EtOH}$ ,  $\text{CHCl}_3$  or water;
- tetrakis(4-pyridyl)porphine in  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$ ;
- dicyanonaphthalene (DCN), dicyanoanthracene (DCA) or dicyanobenzene (DCB);
- 10 -  $\text{N,N'$ -dimethyl-2,7-diazapyrenium ( $\text{DAP}^{2+}$ ) bis(tetrafluoroborate).

The reaction is advantageously carried out in the region of room temperature (15 to  $25^\circ\text{C}$ ) under  
15 irradiation, with visible light while sparging with oxygen, for a period which may be from 2 to 8 hours.

The hydroperoxide formed, of formula III, spontaneously decomposes with stirring, especially in the presence of  
20  $\text{Na}_2\text{SO}_4$ .

A subject of the present invention is also the quinoline-5,8-diones of formula:



25

in which:

$\text{R}_1$ ,  $\text{R}_2$  and  $\text{R}_3$  are chosen from hydrogen, a halogen atom,  
30 a  $\text{C}_1$ - $\text{C}_6$  alkyl group,  $-\text{CHO}$ ,  $-\text{OH}$ ,  $-\text{OR}$ ,  $-\text{COOH}$ ,  $-\text{CN}$ ,  $-\text{CO}_2\text{R}$ ,  
 $-\text{CONHR}$ ,  $-\text{CONRR}'$ ,  $-\text{NH}_2$ ,  $-\text{NHCOR}$ ,  
 $-\text{CH}_2\text{N-COOR}$ ,  $\text{CH}_2\text{-N-COOR}$ , morpholino and  $\text{SO}_3\text{H}$ ,  $\text{R}$  and  
 $\text{CH}_2\text{-COOR}'$   $\text{CH}_2\text{-Ar}$

- 5 -

R' being chosen from C<sub>1</sub>-C<sub>6</sub> alkyl groups and Ar being a C<sub>6</sub>-C<sub>14</sub> aryl group,

with the exception of the compounds in which:

R<sub>1</sub> = H, R<sub>2</sub> = H and R<sub>3</sub> is chosen from H, CH<sub>3</sub>, CN and CHO,

5 R<sub>1</sub> = H or CH<sub>3</sub>, R<sub>2</sub> = F and R<sub>3</sub> = H

R<sub>1</sub> = Cl, R<sub>2</sub> = H and R<sub>3</sub> = H

R<sub>1</sub> = OH, R<sub>2</sub> = H and R<sub>3</sub> = COOH, COOCH<sub>3</sub> or CH<sub>3</sub>

R<sub>1</sub> = OH, R<sub>2</sub> = COOH or COOC<sub>2</sub>H<sub>5</sub> and R<sub>3</sub> = H

R<sub>1</sub> = H, R<sub>2</sub> = H and R<sub>3</sub> = OCH<sub>3</sub>

10 R<sub>1</sub> = OH, R<sub>2</sub> = H and R<sub>3</sub> = H

R<sub>1</sub> = OCH<sub>3</sub>, R<sub>2</sub> = H and R<sub>3</sub> = H

R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = H and R<sub>3</sub> = Cl

R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = H and R<sub>3</sub> = CH<sub>3</sub>

## 15 EXAMPLES

Examples of the implementation of the process according to the present invention will be given below.

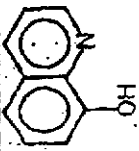
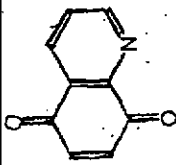
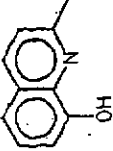
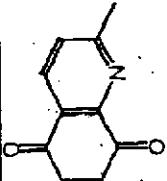
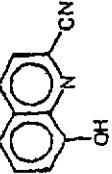
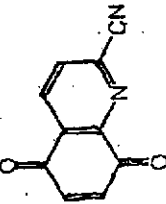
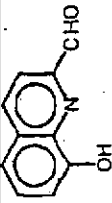
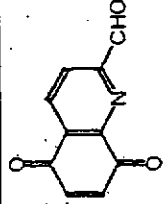
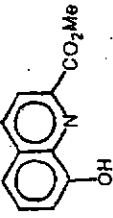
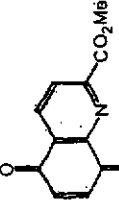
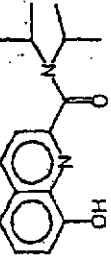
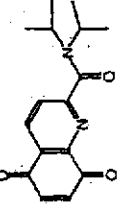
## 20 General procedure

A solution of the compound of formula II (2 mmol) in dichloromethane (or another solvent if insoluble) (20 ml) in a Pyrex flask with flat faces, containing a  
25 catalytic amount of tetraphenylporphine (TPP, 6 mg, i.e. 0.5 mol%), is irradiated at 20°C (cooling with water) with visible light (1500 W xenon arc, filter for radiations > 495 nm) while sparging with oxygen, for 2-8 hours (the reaction is monitored by TLC). The  
30 irradiated solution is then poured onto dry Na<sub>2</sub>SO<sub>4</sub> (3 g), stirred at room temperature for 12 hours and filtered. The solvent is evaporated off and the crude quinone obtained is purified by chromatography on a column of silica.

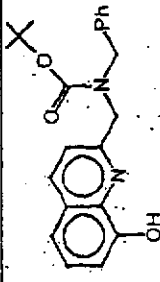
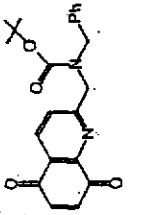
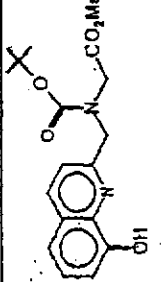
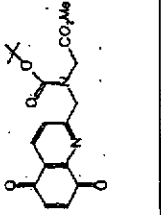
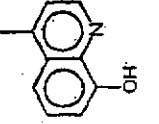
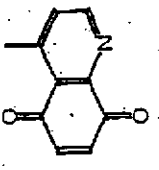
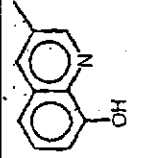
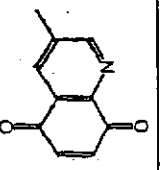
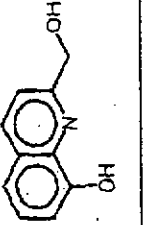
35

The characteristics of the various implementations are collected in the table below.

- 6 -

| Example | Compound II                                                                           | Solvent                         | Time  | Compound II recovered % | Compound I                                                                           | Yield (purification on SiO <sub>2</sub> ) | Yield relative to the converted substrate |
|---------|---------------------------------------------------------------------------------------|---------------------------------|-------|-------------------------|--------------------------------------------------------------------------------------|-------------------------------------------|-------------------------------------------|
| 1       |    | CH <sub>2</sub> Cl <sub>2</sub> | 2h 30 | /                       |     | 82% (95% crude ≈ clean)                   | 82%                                       |
| 2       |    | CH <sub>2</sub> Cl <sub>2</sub> | 2h 30 | /                       |     | 80% (98% crude ≈ clean)                   | 80%                                       |
| 3       |    | CH <sub>2</sub> Cl <sub>2</sub> | 8h    | 15%                     |    | 73%                                       | 86%                                       |
| 4       |   | CH <sub>2</sub> Cl <sub>2</sub> | 5h 30 | 25%                     |   | 51%                                       | 68%                                       |
| 5       |  | CH <sub>2</sub> Cl <sub>2</sub> | 2h    | /                       |  | 81%                                       | 81%                                       |
| 6       |  | CH <sub>2</sub> Cl <sub>2</sub> | 2h    | /                       |  | 89%                                       | 89%                                       |

- 7 -

| Example              | Compound II                                                                           | Solvent                         | Time  | Compound II recovered % | Compound I                                                                         | Yield (purification on SiO <sub>2</sub> ) | Yield relative to the converted substrate |
|----------------------|---------------------------------------------------------------------------------------|---------------------------------|-------|-------------------------|------------------------------------------------------------------------------------|-------------------------------------------|-------------------------------------------|
| 7                    |    | CH <sub>2</sub> Cl <sub>2</sub> | 2h 30 | /                       |  | 53%                                       | 53%                                       |
| 8                    |    | CH <sub>2</sub> Cl <sub>2</sub> | 2h    | 21%                     |  | 50%                                       | 63%                                       |
| 9                    |    | CH <sub>2</sub> Cl <sub>2</sub> | 2h    | /                       |   | 72%                                       | 72%                                       |
| 10                   |   | CH <sub>2</sub> Cl <sub>2</sub> | 2h    | /                       |  | 82%                                       | 82%                                       |
| Com-parative example |  | CH <sub>2</sub> Cl <sub>2</sub> | 2h    | >80%                    |                                                                                    | /                                         | /                                         |

- 8 -

The characteristics of the products obtained will be given below.

Product of example 1:

- 5 - dark yellow solid; m.p. = 120-122°C
- IR (CHCl<sub>3</sub>): 1670 cm<sup>-1</sup>
- <sup>1</sup>H NMR 300 MHz (CDCl<sub>3</sub>): δ 7.08 (d, 1H, J = 11 Hz); 7.18 (d, 1H, J = 11 Hz); 7.73 (m; 1H); 8.44 (m, 1H); 9.07 (m, 1H) ppm
- 10 - <sup>13</sup>C NMR 75 MHz (CDCl<sub>3</sub>): δ 127.9 (d); 129.1 (s); 134.6 (d); 138.0 (d); 139.1 (d); 147.4 (s); 154.8 (d); 183.2 (s); 184.5 (s) ppm.
- MS C<sub>9</sub>H<sub>5</sub>NO<sub>2</sub> (relative intensity): m/z 159 (M<sup>+</sup>, 100); 131 (25); 103 (51).

15

Product of example 2:

- dark yellow solid; m.p. = 135-140°C (decomp.)
- IR (CHCl<sub>3</sub>): 1670 cm<sup>-1</sup>
- <sup>1</sup>H NMR 300 MHz (CDCl<sub>3</sub>): δ 2.80 (s, 3H); 7.03 (d, 1H, J = 11 Hz); 7.13 (d, 1H, J = 11 Hz); 7.58 (d, 1H, J = 8 Hz); 8.30 (d, 1H, J = 8 Hz) ppm.
- 20 - <sup>13</sup>C NMR 75 MHz (CDCl<sub>3</sub>): δ 25.3 (q); 127.0 (s); 127.8 (d); 134.6 (d); 137.9 (d); 138.8 (d); 146.9 (s); 165.2 (s); 183.5 (s); 184.6 (s) ppm.

25

Product of example 3:

- dark green-yellow solid; m.p. = 170-172°C
- IR (CHCl<sub>3</sub>): 2250; 1680 cm<sup>-1</sup>
- <sup>1</sup>H NMR 300 MHz (CDCl<sub>3</sub>): δ 7.20 (d, 1H, J = 11 Hz); 7.30 (d, 1H, J = 11 Hz); 8.12 (d, 1H, J = 8 Hz); 8.64 (d, 1H, J = 8 Hz) ppm
- 30 - <sup>13</sup>C NMR 75 MHz (CDCl<sub>3</sub>): δ 115.7 (s); 130.1 (s); 131.9 (d); 136.4 (d); 138.2 (s); 138.3 (d); 139.7 (d); 147.9 (s); 181.1 (s); 182.8 (s) ppm.

35

Product of example 4:

- dark green-yellow solid; m.p. = 185-187°C
- IR (CHCl<sub>3</sub>): 1720; 1680 cm<sup>-1</sup>

- 9 -

- $^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ ):  $\delta$  7.20 (d, 1H,  $J = 11$  MHz); 7.30 (d, 1H;  $J = 11$  Hz); 8.34 (d, 1H,  $J = 8$  Hz); 8.65 (d, 1H,  $J = 8$  Hz); 10.32 (s, 1H) ppm.
- $^{13}\text{C}$  NMR 75 MHz ( $\text{CDCl}_3$ ):  $\delta$  124.9 (d); 131.2 (s); 136.4 (d); 138.3 (d); 139.6 (d); 147.6 (s); 155.5 (s); 182.4 (s); 183.6 (s); 191.8 (d) ppm.
- MS  $\text{C}_{10}\text{H}_5\text{NO}_3$  (relative intensity):  $m/z$  187 ( $\text{M}^+$ , 17); 159 (100); 103 (32).

## 10 Product of example 5:

- $^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ ):  $\delta$  4.07 (s, 3H); 7.16 (d, 1H,  $J = 10.5$  Hz); 7.27 (d, 1H,  $J = 10.5$  Hz); 8.50 (d, 1H,  $J = 8.1$  Hz); 8.61 (d, 1H,  $J = 8.1$  Hz) ppm.

## 15 Product of example 6:

- $^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ ):  $\delta$  1.25 (d, 6H,  $J = 7.2$  Hz); 1.55 (d, 6H, 7.2 Hz); 3.62 (sept., 1H,  $J = 7.2$  Hz); 3.82 (sept., 1H,  $J = 7.2$  Hz); 7.07 (d, 1H,  $J = 10.5$  Hz); 7.17 (d, 1H,  $J = 10.5$  Hz); 7.88 (d, 1H,  $J = 8.2$  Hz); 8.49 (d, 1H,  $J = 8.2$  Hz) ppm.

## Product of example 7:

- $^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ ): (2 rotamers  $\approx$  50:50)  $\delta$  1.40 and 1.50 (s, 9H); 4.50 and 4.55 (s, 2H); 4.70 and 4.77 (s, 2H); 7.03 (d, 1H,  $J = 10.5$  Hz); 7.14 (d, 1H,  $J = 10.5$  Hz); 7.15-7.35 (m, 5H); 7.48 and 7.61 (d, 1H,  $J = 8.2$  Hz); 8.33 (d, 1H,  $J = 8.2$  Hz) ppm.

## Product of example 8:

- $^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ ): (2 rotamers  $\approx$  50:50)  $\delta$  1.40 and 1.47 (s, 9H); 3.70 and 3.72 (s, 3H); 4.02 and 4.13 (s, 2H); 4.80 and 4.83 (s, 2H); 7.04 and 7.06 (d, 1H,  $J = 10.5$  Hz); 7.13 and 7.15 (d, 1H,  $J = 10.5$  Hz); 7.89 and 7.91 (d, 1H,  $J = 8.3$  Hz); 8.42 and 8.45 (d, 1H,  $J = 8.3$  Hz) ppm.

- 10 -

Product of example 9

- $^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ ):  $\delta$  2.81 (s, 3H); 7.00 (d, 1H,  $J = 10.4$  Hz); 7.11 (d, 1H,  $J = 10.4$  Hz); 7.48 (d, 1H,  $J = 4.9$  Hz); 8.86 (d, 1H,  $J = 4.9$  ppm).
- 5 - MS [ $\text{C}_{10}\text{H}_7\text{NO}_2$ ] (relative intensity):  $m/z$  173 ( $\text{M}^+$ , 100); 145 (53); 117 (23); 91 (28).

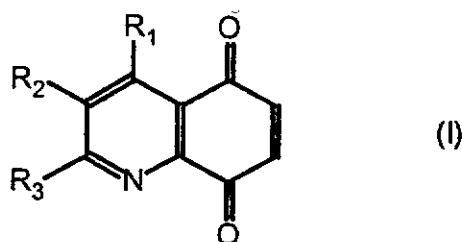
Product of example 10:

- $^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ ):  $\delta$  2.55 (s, 3H); 7.04 (d, 1H,  $J = 10.4$  Hz); 7.14 (d, 1H,  $J = 10.4$  Hz); 8.20 (s, 1H); 8.88 (s, 1H) ppm
- 10 - MS [ $\text{C}_{10}\text{H}_7\text{NO}_2$ ] (relative intensity):  $m/z$  173 ( $\text{M}^+$ , 100); 145 (23); 117 (34); 91 (28).

- 15 It is seen that the success of the process depends strictly on the nature of the starting materials. Thus, for example, a compound of formula II in which  $\text{R}_3$  is a  $-\text{CH}_2\text{OH}$  group is not converted into a product of the formula I, but instead leads to a brown coloration and
- 20 to polymerization.

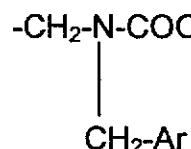
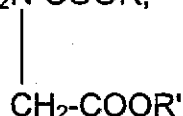
## CLAIMS

1. Process for preparing quinoline-5,8-diones of the formula:



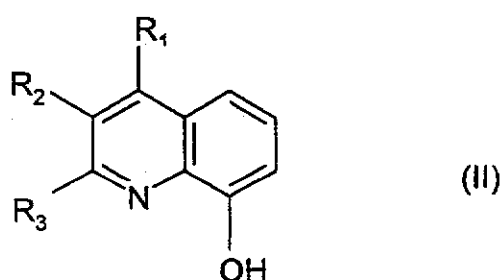
in which:

R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are chosen from hydrogen, a halogen atom, a C<sub>1</sub>-C<sub>6</sub> alkyl group, -CHO, -OH, -OR, -COOH, -CN, -CO<sub>2</sub>R, -CONHR, -CONRR', -NH<sub>2</sub>, -NHCOR, -CH<sub>2</sub>N-COOR, -CH<sub>2</sub>N-COOR, morpholino and SO<sub>3</sub>H,

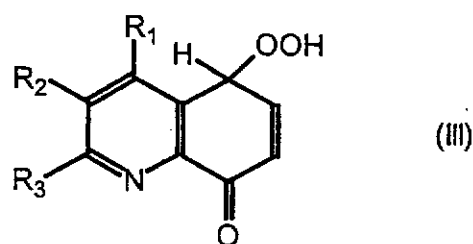


R and R' being chosen from C<sub>1</sub>-C<sub>6</sub> alkyl groups and Ar being a C<sub>6</sub>-C<sub>14</sub> aryl group,

in which an 8-hydroxyquinoline of formula:



in which R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> have the meaning given above, is oxidized with oxygen under the action of actinic radiation in solution in an organic solvent and in the presence of a catalytic amount of a sensitizer, and the hydroperoxide formed, of formula:

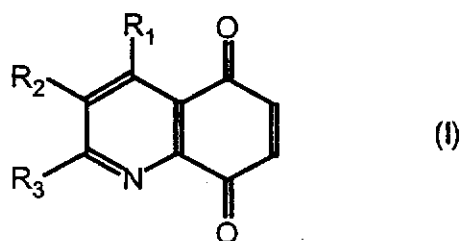


is then decomposed to a compound of formula I.

2. The process as claimed in claim 1, in which the sensitizer is tetraphenylporphine.

5 3. The process as claimed in claim 1 or claim 2, in which the solvent is dichloromethane.

4. A quinoline-5,8-dione of the formula :



10 in which :

R<sub>1</sub>, is chosen from hydrogen, a halogen atom, a -CHO, -OR, -COOH, -CN, -CO<sub>2</sub>R, -CONHR, -CONRR', -NH<sub>2</sub>, -NHCOR,

-CH<sub>2</sub>N-COOR, -CH<sub>2</sub>N-COOR, morpholino

15

CH<sub>2</sub>-COOR'

CH<sub>2</sub>-Ar

and SO<sub>3</sub>H, R and R' being chosen from C<sub>1</sub>-C<sub>6</sub> alkyl groups and Ar being a C<sub>6</sub>-C<sub>14</sub> aryl group,

R<sub>2</sub> is chosen from hydrogen, a halogen atom, a -CHO, -OH, -OR, -COOH, -CN, -CONHR, -CONRR', -NH<sub>2</sub>, -NHCOR,

20

-CH<sub>2</sub>N-COOR, -CH<sub>2</sub>N-COOR, morpholino

CH<sub>2</sub>-COOR'

CH<sub>2</sub>-Ar

25

and  $\text{SO}_3\text{H}$ , R and R' being chosen from  $\text{C}_1\text{-C}_6$  alkyl groups and Ar being a  $\text{C}_6\text{-C}_{14}$  aryl group,

R<sub>3</sub> is chosen from hydrogen, a halogen atom, a  $\text{C}_1\text{-C}_6$  alkyl group,  
 5 -CHO, -OR, -COOH, -CN, -CONHR, -CONRR', -NH<sub>2</sub>, -NHCOR,  
 -CH<sub>2</sub>N-COOR, -CH<sub>2</sub>N-COOR, morpholino  
     |                      |  
   CH<sub>2</sub>-COOR'        CH<sub>2</sub>-Ar

10 and  $\text{SO}_3\text{H}$ , R and R' being chosen from  $\text{C}_1\text{-C}_6$  alkyl groups and Ar being a  $\text{C}_6\text{-C}_{14}$  aryl group,

with the exception of the compounds in which :

R<sub>1</sub> = H, R<sub>2</sub> = H and R<sub>3</sub> is chosen from H, CH<sub>3</sub>, CN and CHO.

15 R<sub>1</sub> = H or CH<sub>3</sub>, R<sub>2</sub> = F and R<sub>3</sub> = H

R<sub>1</sub> = Cl, R<sub>2</sub> = H and R<sub>3</sub> = H

R<sub>1</sub> = OH, R<sub>2</sub> = H and R<sub>3</sub> = COOH, COOCH<sub>3</sub> or CH<sub>3</sub>

R<sub>1</sub> = OH, R<sub>2</sub> = COOH or COOC<sub>2</sub>H<sub>5</sub> and R<sub>3</sub> = H

R<sub>1</sub> = H, R<sub>2</sub> = H and R<sub>3</sub> = OCH<sub>3</sub>

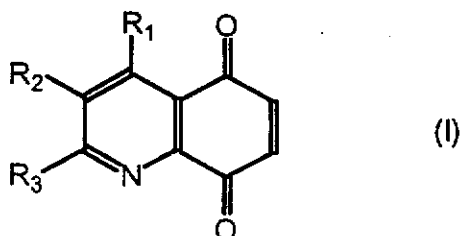
20 R<sub>1</sub> = OH, R<sub>2</sub> = H and R<sub>3</sub> = H

R<sub>1</sub> = OCH<sub>3</sub>, R<sub>2</sub> = H and R<sub>3</sub> = H

R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = H and R<sub>3</sub> = Cl

R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = H and R<sub>3</sub> = CH<sub>3</sub>

25 5. A quinoline-5,8-dione of the formula I :

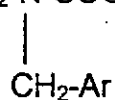
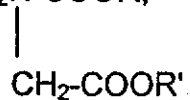


30 in which :

$R_1, R_2$  are chosen from hydrogen, a halogen atom, a  $C_1-C_6$  alkyl group,  $-CHO$ ,  $-OH$ ,  $-OR$ ,  $-COOH$ ,  $-CN$ ,  $-CO_2R$ ,  $-CONHR$ ,  $-CONRR'$ ,  $-NH_2$ ,  $-NHCOR$ ,

$-CH_2N-COOR$ ,  $-CH_2N-COOR$ , morpholino

5



and  $SO_3H$ ,  $R$  and  $R'$  being chosen from  $C_1-C_6$  alkyl groups and  $Ar$  being a  $C_6-C_{14}$  aryl group,

10

$R_3$  is chosen from the groups  $CONRR'$  and  $-CH_2N-COOR$ , et

