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(54) Titre : PROCEDE DE PREPARATION DE COMPOSES CARBONYLE OXYDES A LA POSITION  $\alpha$   
(54) Title: METHOD FOR PRODUCING CARBONYL COMPOUNDS WHICH ARE OXIDIZED IN POSITION  $\alpha$

(57) **Abrégé/Abstract:**

A method for producing compounds which are oxidized in an alpha position by electrochemical reaction with alcohol in the presence of an auxiliary electrolyte and catalytic amounts of a metal salt.

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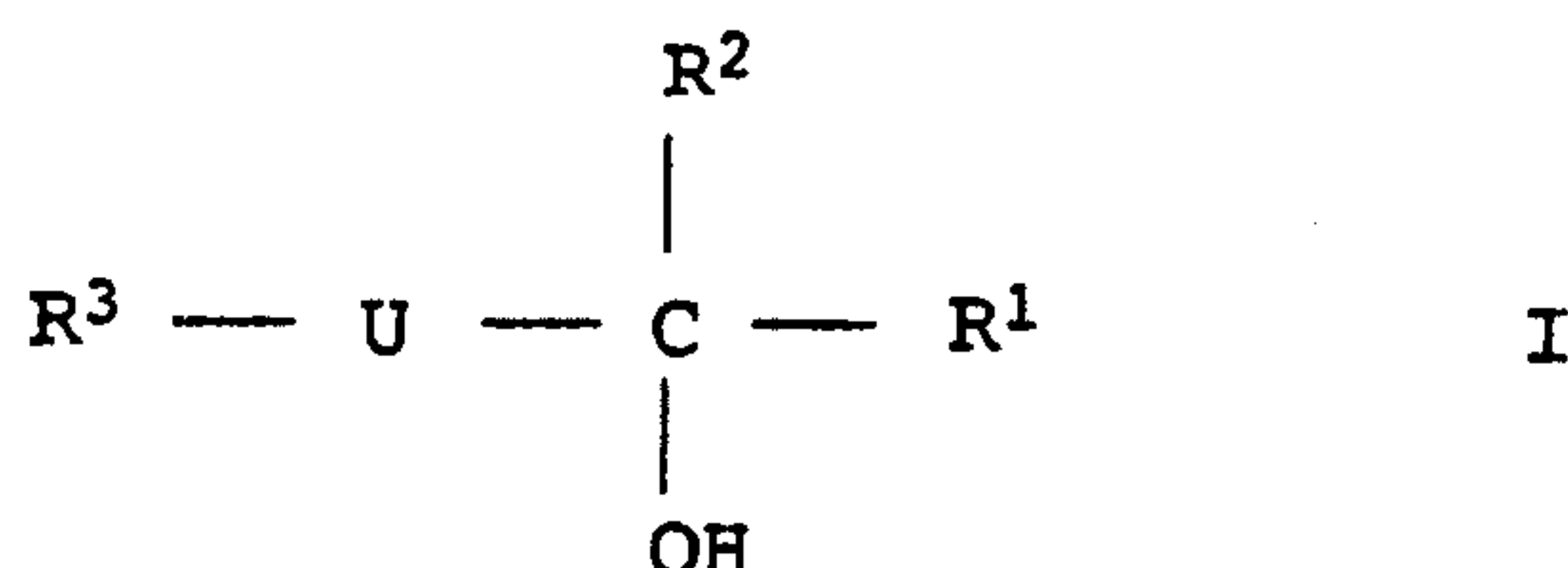
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(54) Title: METHOD FOR PRODUCING CARBONYL COMPOUNDS WHICH ARE OXIDIZED IN POSITION  $\alpha$ (54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON IN  $\alpha$ -STELLUNG OXIDIERTEN CARBONYLVERBINDUN-  
GEN(57) Abstract: A method for producing compounds which are oxidized in an alpha position by electrochemical reaction with alcohol  
in the presence of an auxiliary electrolyte and catalytic amounts of a metal salt.(57) Zusammenfassung: Verfahren zur Herstellung von in alpha-Stellung oxidierten Carbonylverbindungen durch elektrochemi-  
sche Umsetzung mit einem Alkohol in Gegenwart eines Hilfselektrolyten und katalytischen Mengen eines Metallsalzes.

METHOD FOR PRODUCING CARBONYL COMPOUNDSWHICH ARE OXIDIZED IN POSITION  $\alpha$ 

The present invention relates to a process for the preparation of a compound of the general formula I



- 10 where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  are hydrogen,  $\text{C}_1$ - to  $\text{C}_{20}$ -alkyl,  $\text{C}_2$ - to  $\text{C}_{20}$ -alkenyl,  $\text{C}_2$ - to  $\text{C}_{20}$ -alkynyl,  $\text{C}_3$ - to  $\text{C}_{12}$ -cycloalkyl,  $\text{C}_4$ - to  $\text{C}_{20}$ -cycloalkyl-alkyl,  $\text{C}_1$ - to  $\text{C}_{20}$ -hydroxyalkyl, or aryl or  $\text{C}_7$ - to  $\text{C}_{20}$ -arylalkyl which is unsubstituted or substituted by  $\text{C}_1$ - to  $\text{C}_8$ -alkyl,  $\text{C}_1$ - to  $\text{C}_8$ -alkoxy, halogen,  $\text{C}_1$ - to  $\text{C}_4$ -haloalkyl,  $\text{C}_1$ - to  $\text{C}_4$ -haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl,  $\text{C}_2$ - to  $\text{C}_8$ -alkoxycarbonyl or cyano, or  $\text{R}^1$  and  $\text{R}^2$  or  $\text{R}^3$  together are a  $\text{C}_2$ - to  $\text{C}_9$ -alkanediyl unit which is unsubstituted, monosubstituted or disubstituted by  $\text{C}_1$ - to  $\text{C}_8$ -alkyl,  $\text{C}_1$ - to  $\text{C}_8$ -alkoxy and/or halogen and in which one or two methyl groups may also be replaced by a  $(\text{CH}=\text{CH})$  unit and  $\text{R}^3$  is additionally an acetylated carbonyl group in which the alkoxy groups are derived from an alcohol of the general formula II



where  $\text{R}^4$  is  $\text{C}_1$ - to  $\text{C}_6$ -alkyl, and

U is an acetylated carbonyl group in which the alkoxy groups are derived from an alcohol of the general formula II, or is a compound of the general formula III



- 30 where  $\text{R}^1$  is as defined under the formula I, and  $\text{R}^3$  is exclusively aryl which is unsubstituted or substituted by  $\text{C}_1$ - to  $\text{C}_8$ -alkyl,  $\text{C}_1$ - to  $\text{C}_8$ -alkoxy, halogen,  $\text{C}_1$ - to  $\text{C}_4$ -haloalkyl,  $\text{C}_1$ - to  $\text{C}_4$ -haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl,  $\text{C}_2$ - to  $\text{C}_8$ -alkoxycarbonyl or cyano,

V is a carbonyl group or is as defined for U under the formula I, and

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W is as defined for V, with the proviso that one of the groups V and W is a carbonyl group and the other is an acetylated carbonyl group,

5 or

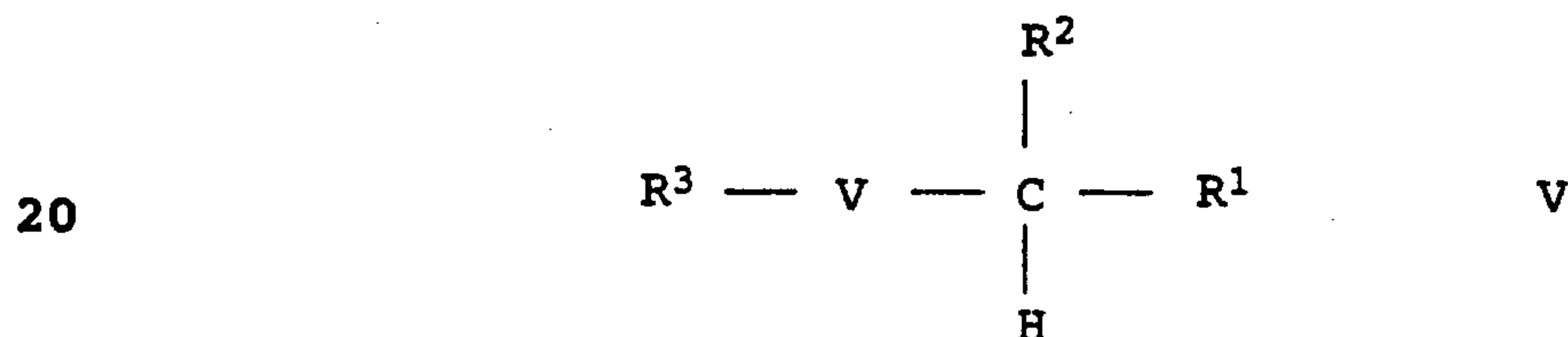
a compound of the general formula IV



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where  $R^4$  is as defined under the formula II, V and W are as defined under the formula II, and  $R^3$  is as defined under the formula III,

15 by subjecting a compound of the general formula V



where V,  $R^1$ ,  $R^2$  and  $R^3$  are as defined under the formula I or III, 25 with the proviso that

- in the case where a compound of the formula III is desired, use is only made of a compound Va in which

30  $R^1$  is exclusively hydrogen and

$R^3$  is exclusively aryl which is unsubstituted or substituted by  $C_1$ - to  $C_8$ -alkyl,  $C_1$ - to  $C_8$ -alkoxy, halogen,  $C_1$ - to  $C_4$ -haloalkyl,  $C_1$ - to  $C_4$ -haloalkoxy, phenyl, phenoxy, 35 halophenyl, halophenoxy, carboxyl,  $C_2$ - to  $C_8$ -alkoxycarbonyl or cyano, and

- in the case where a compound of the formula IV is desired, use is only made of a compound Vb in which

40

$R^1$  and  $R^2$  are exclusively hydrogen,

$R^3$  is exclusively aryl which is unsubstituted or substituted by  $C_1$ - to  $C_8$ -alkyl,  $C_1$ - to  $C_8$ -alkoxy, halogen,  $C_1$ - to 45  $C_4$ -haloalkyl,  $C_1$ - to  $C_4$ -haloalkoxy, phenyl, phenoxy,

## 3

halophenyl, halophenoxy, carboxyl, C<sub>2</sub>- to  
C<sub>8</sub>-alkoxycarbonyl or cyano,

to an electrochemical reaction with an alcohol of the general  
5 formula II in the presence of an auxiliary electrolyte and  
catalytic amounts of a metal salt (S) derived from a metal from  
the 1st, 2nd, 6th or 8th sub-group or from lead, tin or rhenium.

EP-A-460 451 discloses a process for the preparation of  
10  $\alpha$ -hydroxymethyl ketals by electrochemical oxidation of aldehydes  
or ketones in the presence of alcohols and halogen compounds as  
auxiliary electrolytes. Repetition of the examples shows that  
more highly oxidized carbonyl compounds are also formed under the  
process conditions described if the carbonyl group is in the  
15  $\alpha$ -position to an aromatic radical. Thus, for example, a methylene  
group in the  $\alpha$ -position to the carbonyl group can be oxidized to  
the carbonyl function and in addition the aldehyde or keto  
carbonyl group originally present can be oxidized to the carboxyl  
group. Thus, it is not only  $\alpha$ -hydroxyketals that are formed, but  
20 also  $\alpha$ -ketaldehydes,  $\alpha$ -ketoacetals,  $\alpha$ -ketalcarboxylic esters and  
 $\alpha$ -keto orthoesters. However, this process is still not entirely  
satisfactory since the overall yield of these target products is  
relatively low and in addition large amounts of other  
substantially unusable products are formed.

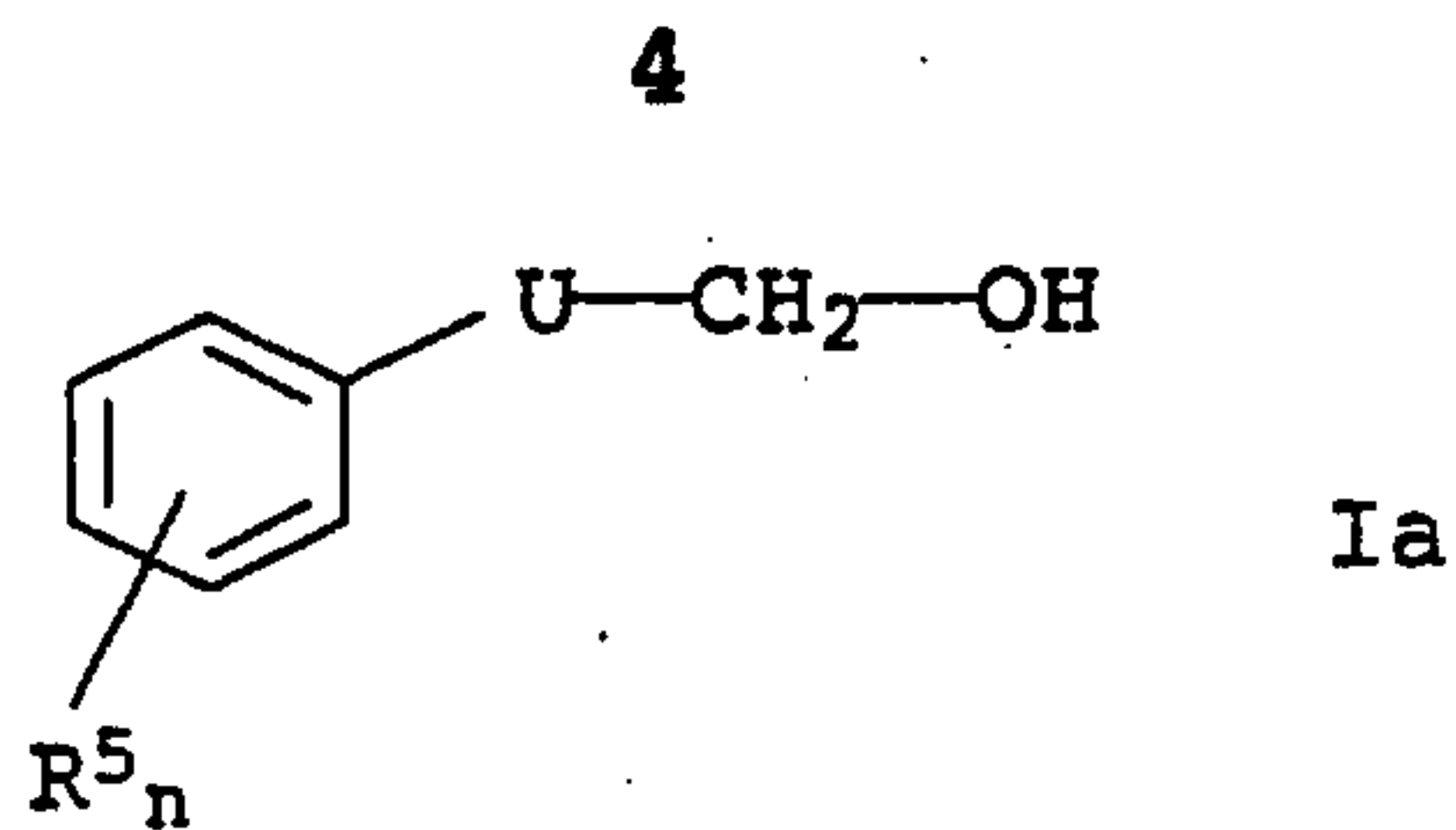
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German Patent Application 19904929, which is not a prior  
publication, relates to a process for the preparation of  
2,2,3,3-tetramethoxypropanol by electrochemical oxidation of  
methylglyoxal dimethyl acetal using a mixture comprising  
30 methanol, water and an auxiliary electrolyte as electrolysis  
medium and an iron, steel, platinum or zinc cathode.

It is an object of the present invention to provide an  
electrochemical process by means of which  $\alpha$ -hydroxyketals,  
35  $\alpha$ -ketalaldehydes,  $\alpha$ -ketoacetals,  $\alpha$ -ketalcarboxylic esters and  
 $\alpha$ -keto orthoesters can be prepared from keto or aldehyde carbonyl  
compounds. We have found that this object is achieved by the  
process defined above.

40 The process according to the invention is particularly suitable  
for the preparation of compounds of the general formulae I, III  
and IV, where the radical R<sup>4</sup> in the acetylated carbonyl group is  
derived from methanol or ethanol.

45 Of the compounds of the formula I, preference is given to those  
of the formula Ia

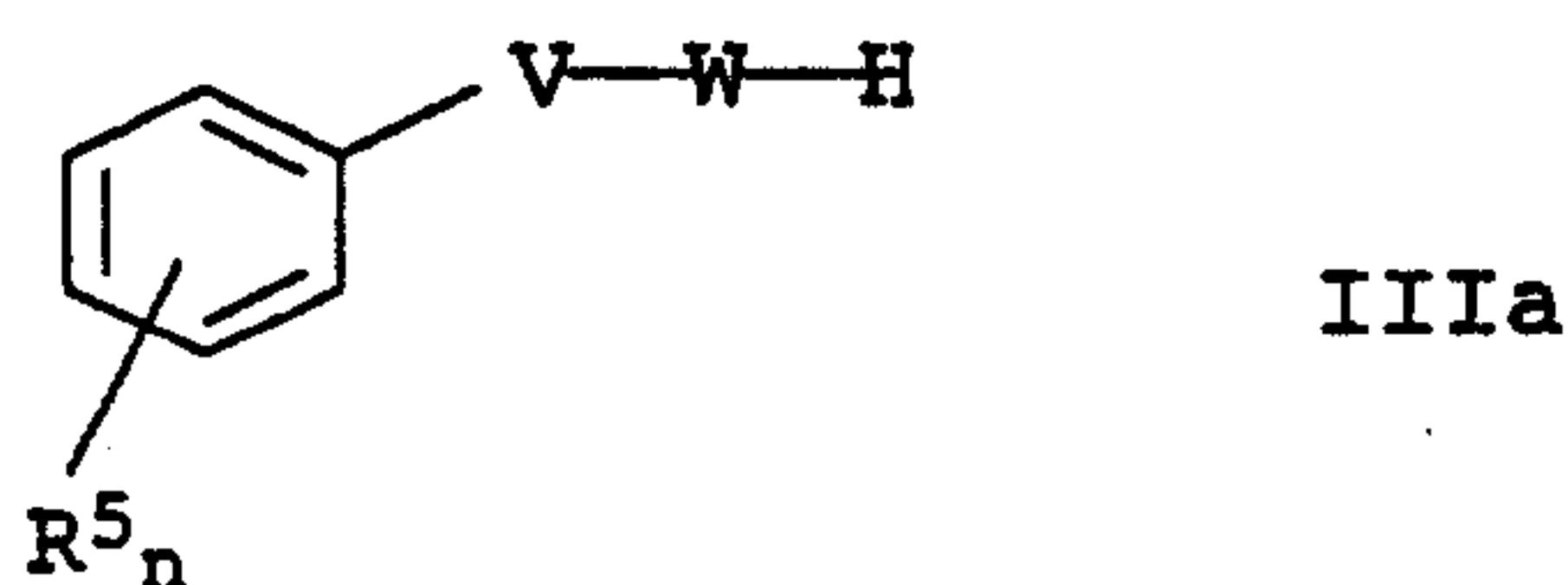


where U is as defined in formula I,

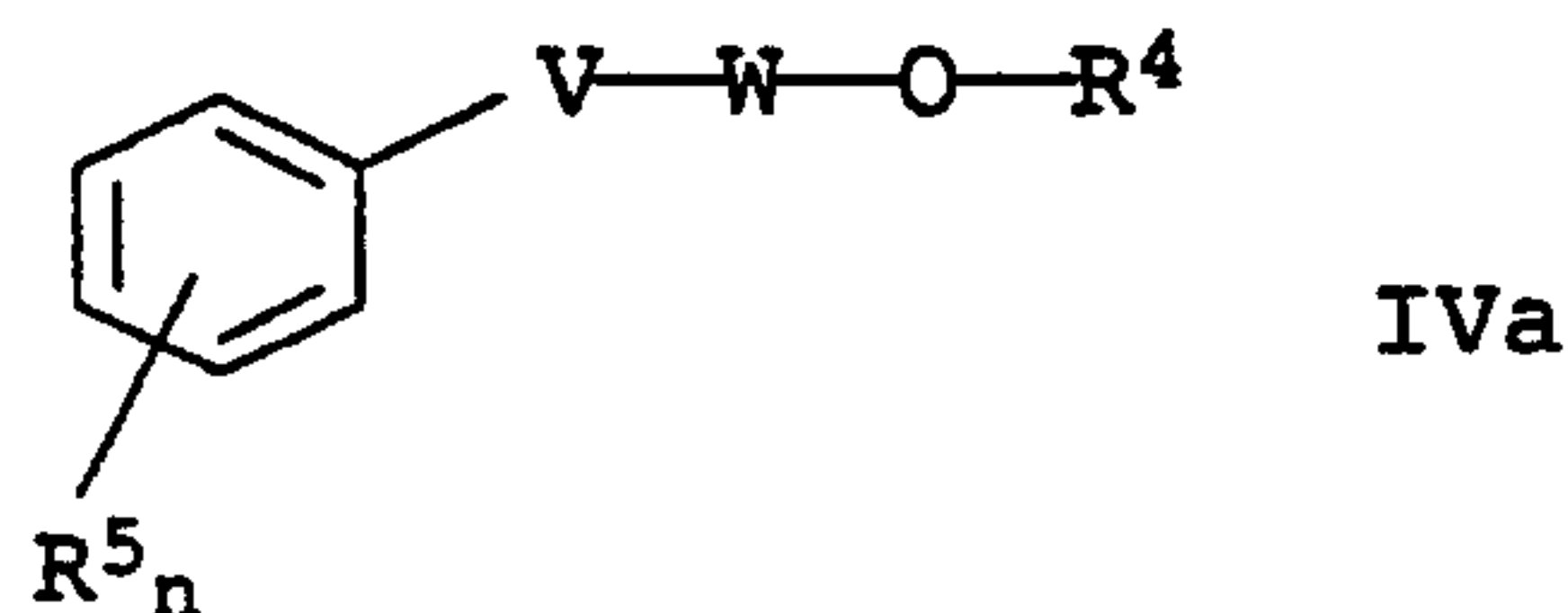
n is 0, 1, 2 or 3, and

$R^5$  is  $C_1$ - to  $C_8$ -alkyl,  $C_1$ - to  $C_8$ -alkoxy, halogen,  $C_1$ - to  $C_4$ -haloalkyl,  $C_1$ - to  $C_4$ -haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl,  $C_2$ - to  $C_8$ -alkoxycarbonyl or cyano.

Preference is likewise given to compounds of the general formula IIIa

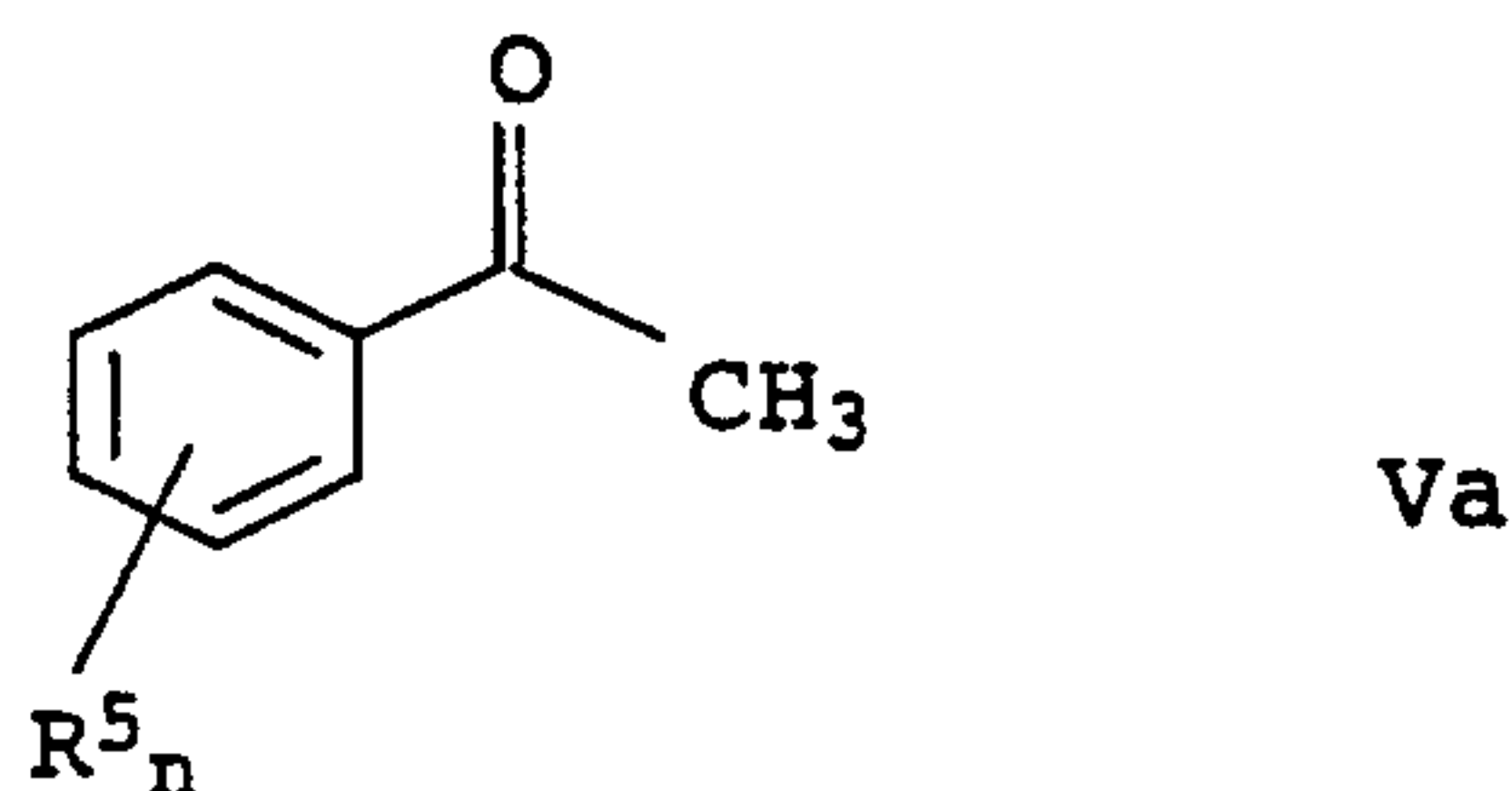


where n, V, W and  $R^5$  are as defined under the formula Ia or III, or of the general formula IVa



where n, V, W,  $R^4$  and  $R^5$  are as defined under the formula Ia or IIIa.

These compounds are prepared by employing as starting compound of the general formula V a compound of the general formula Va



5

where n and R<sup>5</sup> are as defined under the formula Ia.

The process is furthermore particularly suitable for the preparation of compounds of the general formula Ib

5



where m is a number from 1 to 10, and R<sup>4</sup> is as defined in formula II, and for whose preparation use is made of a compound of the  
10 general formula Vb



The process is very particularly suitable for the preparation of  
15

- 2-phenyl-2,2-dimethoxyethanol,  
2-phenyl-2,2-dimethoxyacetaldehyde and 2-phenylglyoxal  
dimethyl acetal from methanol and acetophenone
- 20 -  $\alpha$ -hydroxyoctanal dimethyl acetal from octanal and
- 2,2,3,3-tetramethoxypropanol from methylglyoxal dimethyl  
acetal.
- 25 The auxiliary electrolyte present in the electrolysis solution is  
generally a halogen-containing auxiliary electrolyte, such as  
elemental halogen, an alkyl halide or a hydrogen halide.  
Halogen-containing salts, in particular iodides or bromides, can  
also preferably be employed. Examples are ammonium halides, such  
30 as ammonium bromide, ammonium iodide and tetrabutylammonium  
iodide. Particularly preferred metal halides are furthermore  
alkali metal halides, such as sodium bromide, sodium iodide,  
potassium iodide and potassium bromide.
- 35 The metal salts (S) are preferably those derived from mineral  
acids. The anions of the metal salt are thus, for example,  
phosphate, sulfate, nitrate, perchlorate or halide.
- The cations of the metal salt (S) are preferably iron, nickel,  
40 platinum, palladium, cobalt, zinc, silver or copper ions. The  
metal salt (S) is generally added to the electrolysis solution in  
amounts such that its metal ions are present therein in amounts  
of from 1 to 1000 ppm by weight, preferably from 5 to 500 ppm by  
weight, particularly preferably from 5 to 300 ppm by weight,  
45 based on the total amount of electrolysis liquid.

## 6

If desired, conventional co-solvents are added to the electrolysis liquid. These are the inert solvents having a high oxidation potential which are generally conventional in organic chemistry. Examples which may be mentioned are dimethyl carbonate  
5 and propylene carbonate. Besides said co-solvents, water can also be added to the electrolysis liquid, although the water content should not exceed 5% by weight, based on the total amount of electrolysis liquid.

10 In general, the electrolysis liquid has the following composition:

- a starting compound of the general formula V
- 15 - an alcohol of the general formula II
- a halogen-containing auxiliary electrolyte
- catalytic amounts of the metal salt (S)
- 20 - possibly the desired products of the general formulae I, III and IV
- possibly other by-products of electrolysis which are derived  
25 from the compounds of the general formulae I, II, III, IV and V
- if desired, other conventional co-solvents.

30 The ratio between the products of the general formulae I and V and the other by-products to the starting compounds in the electrolysis liquid and the ratio of the individual products having different degrees of oxidation to one another is of course, dependent on the progress of the reaction.

35 The ratio between the products of the general formulae I, III, IV and V and the other by-products to the starting compounds in the electrolysis liquid and the ratio of the individual products having different degrees of oxidation to one another is of course  
40 dependent on the progress of the reaction.

In general, the amount of charge expended for the reaction is from 1 to 7 F per mole of starting compound of the general formula V. From 3.5 to 4 F are preferably employed if mixtures  
45 are desired which are intended to contain, as principal components, compounds of the formulae I and III, and from 4.5 to 5.5 F are employed if mixtures are desired which are intended to

## 7

contain, as principal components, compounds of the formulae I and IV.

The process according to the invention can be carried out in all conventional types of electrolysis cell. Preference is given to undivided flow cells.

The current densities at which the process is carried out are generally from 0.5 to 25 A/dm<sup>2</sup>. The temperatures are usually from -20 to 60°C, preferably from 0 to 60°C. The process is generally carried out at atmospheric pressure. Higher pressures are preferably used if higher temperatures are to be used in order to prevent the starting compounds or co-solvents from boiling.

15 Examples of suitable anode materials are noble metals such as platinum, or metal oxides, such as ruthenium or chromium oxide, or mixtures of the RuO<sub>x</sub>/TiO<sub>x</sub> type. Preference is given to graphite or carbon electrodes.

20 Suitable cathode materials are generally iron, steel, nickel, and noble metals, such as platinum and graphite and carbon materials.

When the reaction is complete, the electrolysis liquid is worked up by general separation methods. To this end, the electrolysis liquid is generally first distilled, and the individual compounds are obtained separately in the form of different fractions. Further purification can be carried out, for example, by crystallization or chromatography.

### 30 Experimental part

All experiments were carried out in an undivided cell having 11 bipolar electrodes (10 gaps, gap separation 1.5 mm).

35 Current density: 3.4 A/dm<sup>2</sup>

Flow rate: 400 l/h

#### Example 1:

40

Batch:

450 g of acetophenone  
30 g of potassium iodide  
2460 g of methanol  
Fe(III): 5 ppm

45 Cathode:

steel 1.4301

Anode:

graphite

Duration:

7.03 h

8

Temperature: 36°C  
Amount of charge: 3.5 F  
Current strength: 5 A  
Conversion: >99%

5 Yields of the target products:  
2-phenyl-2,2-dimethoxyethanol: 24%  
2-phenyl-2,2-dimethoxyacetaldehyde: 42%  
2-phenylglyoxal dimethyl acetal: 0%  
phenylglyoxylic acid methyl orthoester and methyl  
10 2-phenyl-2,2-dimethoxy acetate: 0%  
Total: 66%

## Example 2:

15 Batch: 450 g of acetophenone  
30 g of potassium iodide  
2460 g of methanol  
Fe(III): 5 ppm  
Cathode: Graphite  
20 Anode: Graphite  
Duration: 7.03 h  
Temperature: 36°C  
Amount of charge: 3.5 F  
Current strength: 5 A  
25 Conversion: 84%

## Yields of the target products:

2-phenyl-2,2-dimethoxyethanol: 15%  
30 2-phenyl-2,2-dimethoxyacetaldehyde: 24%  
2-phenylglyoxal dimethyl acetal: 8%  
phenylglyoxylic acid methyl orthoester and methyl  
2-phenyl-2,2-dimethoxy acetate: 3%  
Total: 50%

35

## Example 3 (4118/98-176):

Batch: 450 g of acetophenone  
90 g of potassium iodide  
40 2460 g of methanol  
Fe(III): 5 ppm  
Cathode: steel 1.4301  
Anode: graphite  
Duration: 7.03 h  
45 Temperature: 55-58°C  
Amount of charge: 3.5 F  
Current strength: 5 A

9

Conversion: 88%  
Yields of the target products:  
2-phenyl-2,2-dimethoxyethanol: 38%  
2-phenyl-2,2-dimethoxyacetaldehyde: 19%  
5 2-phenylglyoxal dimethyl acetal: 12%  
phenylglyoxylic acid methyl orthoester and methyl  
2-phenyl-2,2-dimethoxy acetate: 1%  
Total: 70%

## 10 Example 4:

Batch: 450 g of acetophenone  
90 g of potassium iodide  
2460 g of methanol  
15 Fe(III): 5 ppm  
Cathode: steel 1.4301  
Anode: graphite  
Duration: 10.47 h  
Temperature: 55-58°C  
20 Amount of charge: 5.5 F  
Current strength: 5 A  
Conversion: >99%  
Yields of the target products:  
2-phenyl-2,2-dimethoxyethanol: 39%  
25 2-phenyl-2,2-dimethoxyacetaldehyde: 0%  
2-phenylglyoxal dimethyl acetal: 3%  
phenylglyoxylic acid methyl orthoester and methyl  
2-phenyl-2,2-dimethoxy acetate: 39%

## 30 Example 5:

Batch: 450 g of octanal  
90 g of potassium iodide  
2460 g of methanol  
35 Fe(III): 5 ppm  
Cathode: MKUS-F04 (SGL)  
Anode: Graphite felt RVG 2003, 6 mm  
(Deutsche Carbon)  
Duration: 3.76 h  
40 Temperature: 55-58°C  
Amount of charge: 2 F  
Current strength: 5 A  
Conversion: >99%  
Yield: 37%  $\alpha$ -hydroxyoctanal dimethyl  
45 acetal

## 10

## Example 6:

Batch: 450 g of octanal  
90 g of potassium iodide  
2460 g of methanol  
Fe(III): 5 ppm  
Cathode: MKUS-F04 (SGL)  
Anode: Graphite felt RVG 2003, 6 mm  
(Deutsche Carbon)  
10 Duration: 3.76 h  
Temperature: 26-28°C  
Amount of charge: 2 F  
Current strength: 5 A  
Conversion: 97%  
15 Yield: 45%  $\alpha$ -hydroxyoctanal  
dimethyl acetal

## Example 7:

20 Batch: 450 g of methylglyoxal  
dimethyl acetal  
45 g of potassium iodide  
2505 g of methanol  
0.11 g NiSO<sub>4</sub>  
25 Cathode: graphite  
Anode: graphite  
Duration: 5 h  
Temperature: 30°C  
Current strength: 5 A  
30 Conversion: 52%  
Selectivity: 59.4%  
Yield of 2,2,3,3-tetramethoxypropanol: 31%

## Comparative Example 1:

35 Batch: 450 g of acetophenone  
30 g of potassium iodide  
2460 g of methanol  
Cathode: steel 1.4301  
40 Anode: graphite  
Duration: 7,03 h  
Temperature: 36°C  
Amount of charge: 3.5 F  
Current strength: 5 A  
45 Conversion: 98%  
Yields of the target products:  
2-phenyl-2,2-dimethoxyethanol: 19%

## 11

2-phenyl-2,2-dimethoxyacetaldehyde: 12%  
2-phenylglyoxal dimethyl acetal: 5%  
phenylglyoxylic acid methyl orthoester and methyl  
2-phenyl-2,2-dimethoxy acetate: 9%  
5 Total: 45%

## Comparative Example 2:

Batch: 450 g of acetophenone  
10 30 g of potassium iodide  
2460 g of methanol  
Cathode: graphite  
Anode: graphite  
Duration: 7.03 h  
15 Temperature: 36°C  
Amount of charge: 3.5 F  
Current strength: 5 A  
Conversion: 95%  
Yields of the target products:  
20 2-phenyl-2,2-dimethoxyethanol: 7%  
2-phenyl-2,2-dimethoxyacetaldehyde: 25%  
2-phenylglyoxal dimethyl acetal: 3%  
phenylglyoxylic acid methyl orthoester and methyl  
2-phenyl-2,2-dimethoxy acetate: 1%  
25 Total: 36%

## Comparative Example 3:

Batch: 450 g of octanal  
30 90 g of potassium iodide  
2460 g of methanol  
Cathode: graphite  
Anode: graphite  
Duration: 3.76 h  
35 Temperature: 55-58°C  
Amount of charge: 2 F  
Current strength: 5 A  
Conversion: >99%  
Yield: 30%

40

## Comparative Example 4:

Batch: 450 g of octanal  
45 90 g of potassium iodide  
2460 g of methanol  
Cathode: graphite  
Anode: graphite

12

Duration: 3.76 h  
Temperature: 26-28°C  
Amount of charge: 2 F  
Current strength: 5 A  
5 Conversion: >99%  
Yield: 40%

## Comparative Example 5:

10 Batch: 450 g of methylglyoxal  
dimethyl acetal  
45 g of potassium iodide  
2505 g of methanol.  
Cathode: graphite  
15 Anode: graphite  
Duration: 5 h  
Temperature: 30°C  
Current strength: 5 A  
Conversion: >99%  
20 Selectivity: 24.6%  
Yield: 24.6% 2,2,3,3-tetramethoxypropanol

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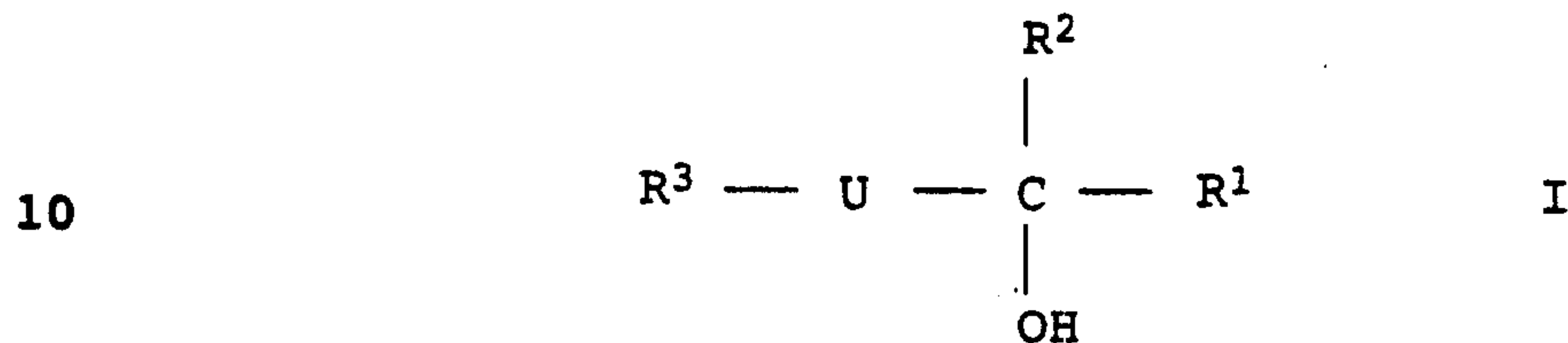
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We claim:

1. A process for the preparation of a compound of the general  
5 formula I



15 where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> are hydrogen, C<sub>1</sub>- to C<sub>20</sub>-alkyl, C<sub>2</sub>- to C<sub>20</sub>-alkenyl, C<sub>2</sub>- to C<sub>20</sub>-alkynyl, C<sub>3</sub>- to C<sub>12</sub>-cycloalkyl, C<sub>4</sub>- to C<sub>20</sub>-cycloalkyl-alkyl, C<sub>1</sub>- to C<sub>20</sub>-hydroxyalkyl, or aryl or C<sub>7</sub>- to C<sub>20</sub>-arylalkyl which is unsubstituted or substituted by C<sub>1</sub>- to C<sub>8</sub>-alkyl, C<sub>1</sub>- to C<sub>8</sub>-alkoxy, halogen, C<sub>1</sub>- to C<sub>4</sub>-haloalkyl, C<sub>1</sub>- to C<sub>4</sub>-haloalkoxy, phenyl, phenoxy, halophenyl,  
20 halophenoxy, carboxyl, C<sub>2</sub>- to C<sub>8</sub>-alkoxycarbonyl or cyano, or R<sup>1</sup> and R<sup>2</sup> or R<sup>3</sup> together are a C<sub>2</sub>- to C<sub>9</sub>-alkandiyl unit which is unsubstituted, monosubstituted or disubstituted by C<sub>1</sub>- to C<sub>8</sub>-alkyl, C<sub>1</sub>- to C<sub>8</sub>-alkoxy and/or halogen and in which one or two methyl groups may also be replaced by a (CH=CH) unit and  
25 R<sup>3</sup> is additionally an acetylated carbonyl group in which the alkoxy groups are derived from an alcohol of the general formula II



where R<sup>4</sup> is C<sub>1</sub>- to C<sub>6</sub>-alkyl, and

U is an acetylated carbonyl group in which the alkoxy groups are derived from an alcohol of the general formula II, or  
35 is a compound of the general formula III



40 where R<sup>1</sup> is as defined under the formula I, and R<sup>3</sup> is exclusively aryl which is unsubstituted or substituted by C<sub>1</sub>- to C<sub>8</sub>-alkyl, C<sub>1</sub>- to C<sub>8</sub>-alkoxy, halogen, C<sub>1</sub>- to C<sub>4</sub>-haloalkyl, C<sub>1</sub>- to C<sub>4</sub>-haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl, C<sub>2</sub>- to C<sub>8</sub>-alkoxycarbonyl or cyano,

45 V is a carbonyl group or is as defined for U under the formula I, and

14

W is as defined for V, with the proviso that one of the groups V and W is a carbonyl group and the other is an acetylated carbonyl group,

5 or

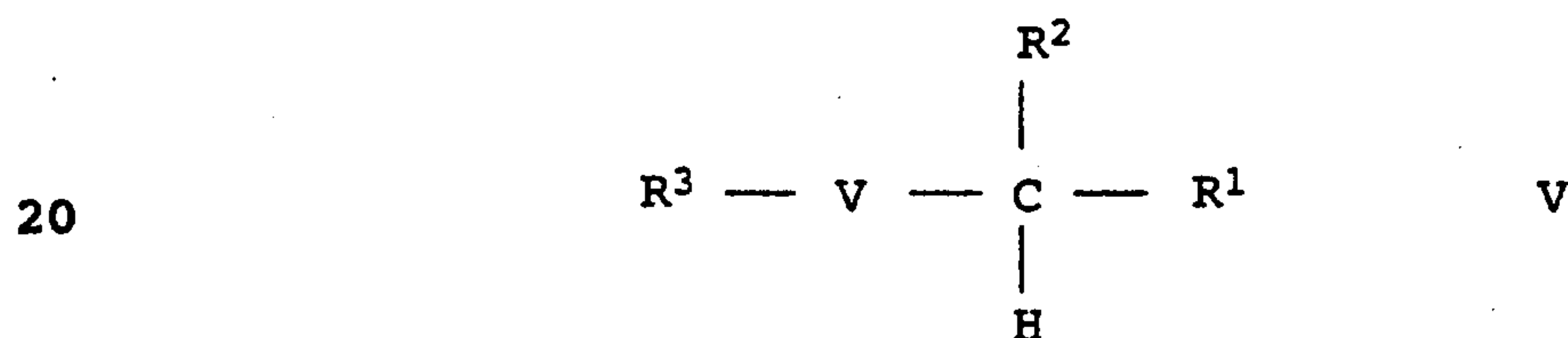
a compound of the general formula IV



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where  $R^4$  is as defined under the formula II, V and W are as defined under the formula II, and  $R^3$  is as defined under the formula III,

15 by subjecting a compound of the general formula V



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25 where V,  $R^1$ ,  $R^2$  and  $R^3$  are as defined under the formula I or III, with the proviso that

- in the case where a compound of the formula III is desired, use is only made of a compound Va in which

30  $R^1$  is exclusively hydrogen and

35  $R^3$  is exclusively aryl which is unsubstituted or substituted by  $C_1$ - to  $C_8$ -alkyl,  $C_1$ - to  $C_8$ -alkoxy, halogen,  $C_1$ - to  $C_4$ -haloalkyl,  $C_1$ - to  $C_4$ -haloalkoxy, phenyl, phenoxy, halophenyl, halophenoxy, carboxyl,  $C_2$ - to  $C_8$ -alkoxycarbonyl or cyano, and

- in the case where a compound of the formula IV is desired, use is only made of a compound Vb in which

40

$R^1$  and  $R^2$  are exclusively hydrogen,

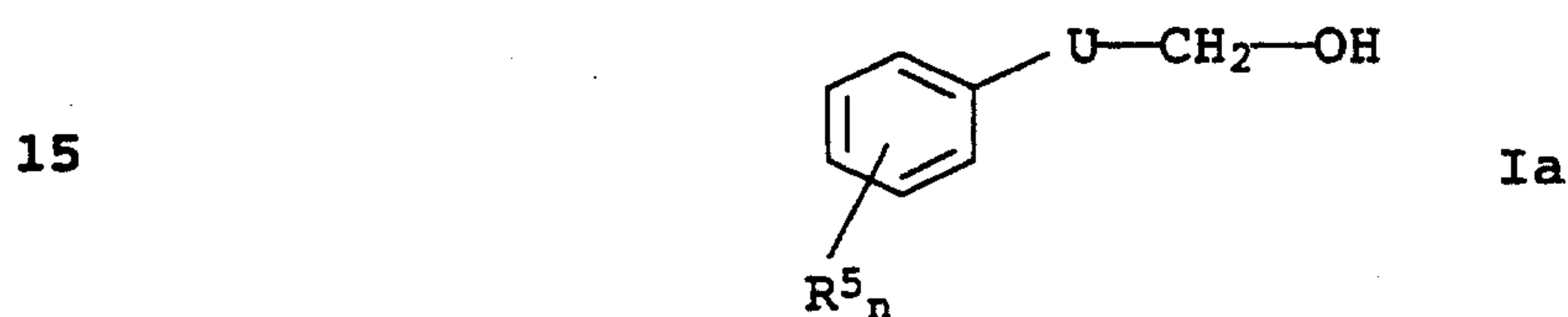
45  $R^3$  is exclusively aryl which is unsubstituted or substituted by  $C_1$ - to  $C_8$ -alkyl,  $C_1$ - to  $C_8$ -alkoxy, halogen,  $C_1$ - to  $C_4$ -haloalkyl,  $C_1$ - to  $C_4$ -haloalkoxy,

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phenyl, phenoxy, halophenyl, halophenoxy, carboxyl,  
C<sub>2</sub>- to C<sub>8</sub>-alkoxycarbonyl or cyano,

to an electrochemical reaction with an alcohol of the general  
formula II in the presence of an auxiliary electrolyte and  
catalytic amounts of a metal salt (S) derived from a metal  
from the 1st, 2nd, 6th or 8th sub-group or from lead, tin or  
rhenium.

- 10 2. A process as claimed in claim 1 for the preparation of a  
compound of the general formula Ia



where U is as defined under the formula I,

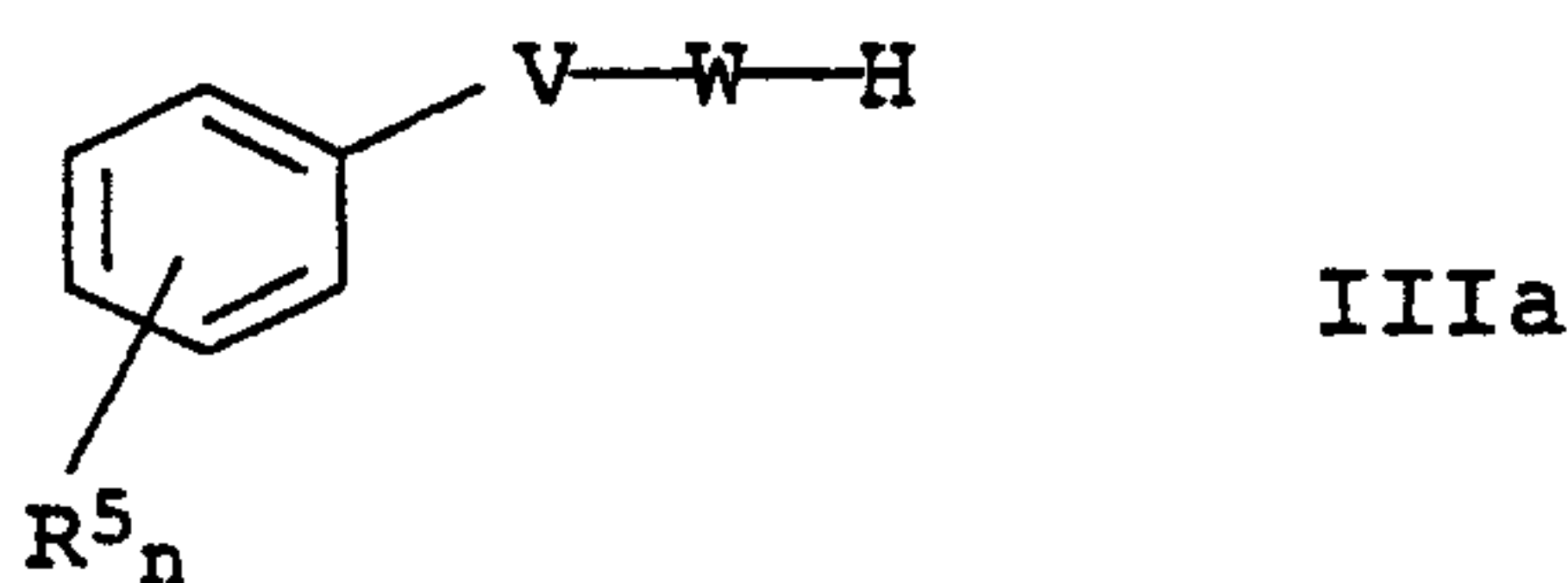
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n is 0, 1, 2 or 3, and

25 R<sup>5</sup> is C<sub>1</sub>- to C<sub>8</sub>-alkyl, C<sub>1</sub>- to C<sub>8</sub>-alkoxy, halogen, C<sub>1</sub>- to  
C<sub>4</sub>-haloalkyl, C<sub>1</sub>- to C<sub>4</sub>-haloalkoxy, phenyl, phenoxy,  
halophenyl, halophenoxy, carboxyl, C<sub>2</sub>- to  
C<sub>8</sub>-alkoxycarbonyl or cyano,

or of the general formula IIIa

30

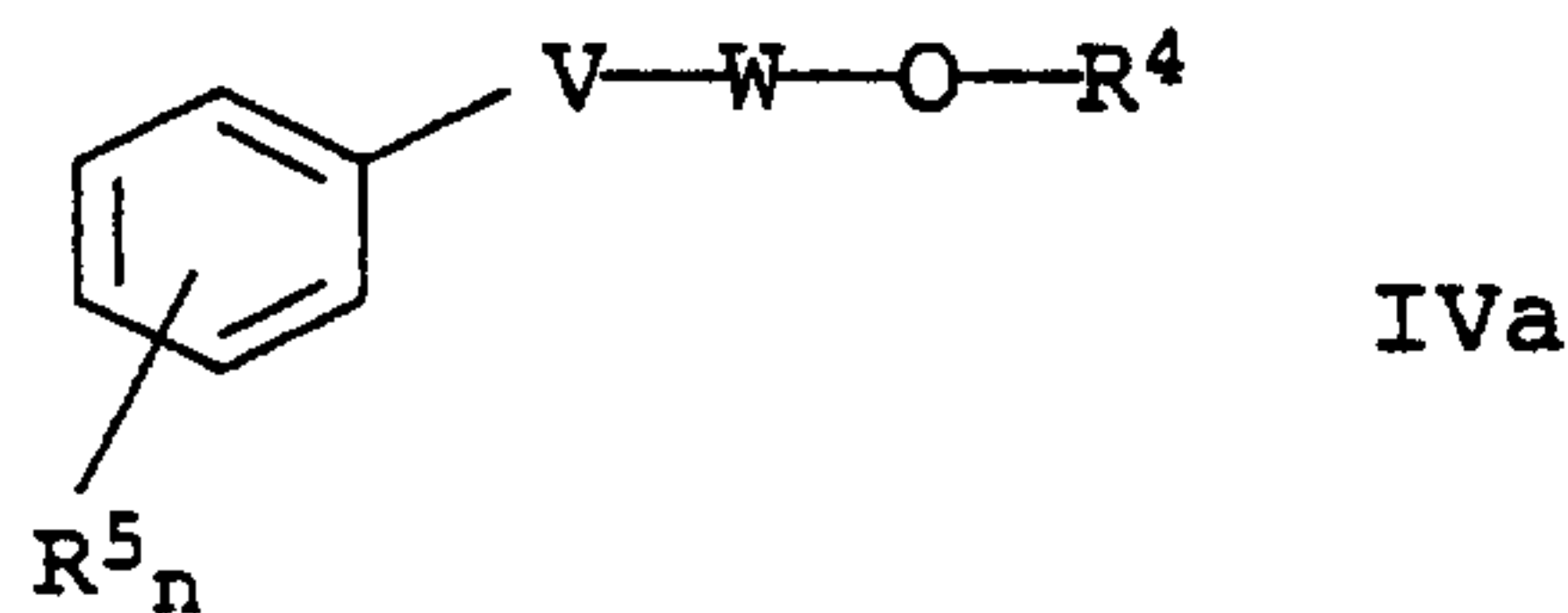


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where n, V, W and R<sup>5</sup> are as defined under the formula Ia or  
III,

or of the general formula IVa

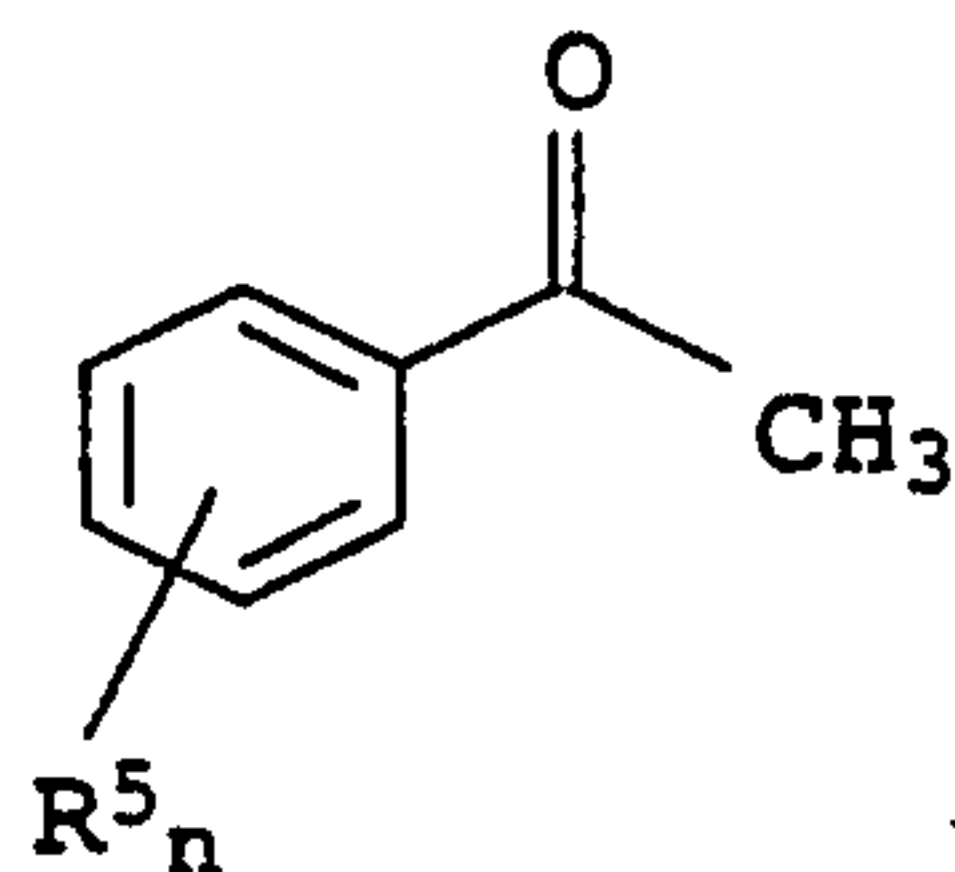
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where n, V, W, R<sup>4</sup> and R<sup>5</sup> are as defined under the formula Ia or IIIa, by employing, as starting compound of the general formula V, a compound of the general formula Va,

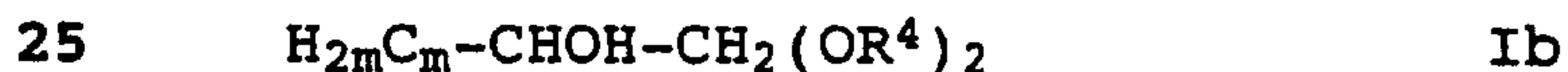


Va

where n and R<sup>5</sup> are as defined under the formula Ia.

3. A process as claimed in claim 2, where the compound of the general formula Ia is 2-phenyl-2,2-dimethoxyethanol, the compound of the general formula IIIa is 2-phenyl-2,2-dimethoxyacetaldehyde or 2-phenylglyoxal dimethyl acetal, the compound of the general formula IVa is phenylglyoxylic acid methyl orthoester, and the compound of the general formula Va is acetophenone.

4. A process as claimed in claim 1, where the compound of the general formula I is a compound of the general formula Ib



where m is a number from 1 to 10, and R<sup>4</sup> is as defined under the formula II, and the compound of the general formula V is a compound of the general formula Vb



5. A process as claimed in any one of claims 1 to 4, where the compound of the formula I is 2,2,3,3-tetramethoxypropanol, and the starting compound employed is methylglyoxal dimethyl acetal.

6. A process as claimed in any one of claims 1 to 5, where the anions of the metal salt (S) are derived from mineral acids.

7. A process as claimed in any one of claims 1 to 6, where the anions of the metal salt (S) are phosphate, sulfate, nitrate, perchlorate or halide.

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8. A process as claimed in any one of claims 1 to 7, where the cations of the metal salt (S) are iron, nickel, platinum, palladium, cobalt, zinc, silver or copper.
- 5 9. A process as claimed in any one of claims 1 to 8, where the electrolysis liquid contains from 1 to 1000 ppm by weight of metal ions of the metal salt (S), based on the total amount of electrolysis liquid.
- 10 10. A process as claimed in any one of claims 1 to 9, where the electrolysis liquid contains a halogen-containing auxiliary electrolyte.
11. A process as claimed in any one of claims 1 to 10, where the  
15 electrolysis liquid essentially consists of
- a starting compound of the general formula V
  - an alcohol of the general formula II
  - 20 - a halogen-containing auxiliary electrolyte
  - catalytic amounts of the metal salt (S)
  - 25 - possibly the desired products of the general formulae I, III and IV
  - possibly other by-products of electrolysis which are derived from the compounds of the general formulae I, II,  
30 III, IV and V, and
  - if desired, other conventional co-solvents.
12. A process as claimed in any one of claims 1 to 11, where  
35
- the proportion of the starting compounds and products of the general formulae I, III, IV and V and of the other by-products of electrolysis from the abovementioned compounds is from 1 to 70% by weight,  
40
  - the proportion of the alcohol of the general formula II is from 14.9 to 94.9% by weight,
  - the proportion of auxiliary electrolyte is from 0.1 to 5%  
45 by weight, and

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- the proportion of any co-solvents present is from 0 to 70% by weight,

based on the electrolysis liquid.

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13. A process as claimed in any one of claims 1 to 12, where the electrolysis is carried out in an undivided electrolysis cell.

- 10 14. A process as claimed in any one of claims 1 to 13, where the anodes employed are made of noble metals, noble-metal oxides, graphite or carbon materials, and the cathodes employed are made of iron, steel, nickel, zinc, noble metals, graphite or carbon materials.

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