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(54) Title: PROCESS FOR THE PRODUCTION OF KETONES

(57) Abstract: Aliphatic or alicyclic monoketones or alicyclic diketones of formula (I): R^1-C(=O)-R^2, wherein R^1 is a linear or branched C_{1-10}-alkyl group and R^2 is a linear or branched C_{1-10}-alkyl group or a phenyl group, or R^1 and R^2 together are $-(CH_2)_m-[C(=O)]_n-(CH_2)_P-$, wherein m and p independently are integers from 1 to 4 and n is 0 or 1, thus forming an alicyclic ring together with the carbonyl group of (I), are produced by oxidizing an alcohol of formula (II): $R^{1'}$-CHOH-$R^{2'}$, in which $R^{1'}$ and $R^{2'}$ either have the same meaning as R^1 and R^2 above or, if R^1 and R^2 together are $-(CH_2)_m-[C(=O]_n-(CH_2)_p-$, are together $-(CH_2)_m-(CHOH)_n-(CH_2)_p-$ wherein m, n and p are as defined above, with a peroxy compound in the presence of a carboxylic acid and a manganese(IV) complex of 1,4,7-trimethyl-1,4,7-triazacyclononane.

Process for the Production of Ketones

The invention relates to a process for the production of aliphatic and alicyclic ketones by oxidizing the corresponding secondary alcohols with a peroxy compound in the presence of a catalyst.

The ketones obtainable by the process of the invention have the general formula

$$R^1–C(=O)–R^2 \qquad (I)$$

in which R^1 is a linear or branched C_{1-10}-alkyl group and R^2 is a linear or branched C_{1-10}-alkyl group or a phenyl group,
or R^1 and R^2 together are $–(CH_2)_m–[C(=O)]_n–(CH_2)_p–$, wherein m and p independently are integers from 1 to 4 and n is 0 or 1, thus forming an alicyclic ring together with the carbonyl group of (I).

These ketones are valuable compounds for a large number of applications, for example as solvents, building blocks for organic syntheses, fragrances etc.

Linear or branched C_{1-10}-alkyl groups are, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, *sec*-butyl, *tert*-butyl, pentyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, hexyl, heptyl, octyl, nonyl and decyl, including all isomers of these groups.
The ketones wherein R^1 and R^2 together are a group of the formula $–(CH_2)_m–[C(=O)]_n–(CH_2)_p–$ are in particular all alicyclic monoketones having 3 to 9 ring carbon atoms or diketones having 4 to 10 carbon atoms wherein the carbonyl groups are separated by at least one methylene group. These alicyclic ketones include cyclopropanone, cyclobutanone, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, cyclononanone, 1,3-cyclobutanedione, 1,3-cyclopentanedione, 1,3-cyclohexanedione, 1,4-cyclohexanedione, 1,3-cycloheptanedione, 1,4-cycloheptanedione, 1,3-cyclooctanedione, 1,4-cyclooctanedione, 1,5-cyclooctanedione, 1,3-cyclononandione, 1,4-cyclononanedione, 1,5-cyclononanedione, 1,3-cyclodecanedione, 1,4-cyclodecanedione, 1,5-cyclodecanedione and 1,6-cyclodecanedione.

While some of the above mentioned ketones (I) are being produced by the chemical industry in large amounts (e. g. acetone, cyclohexanone) using processes giving good yields, some others are only available by tedious procedures and/or in poor yields. The object of the present invention was to provide a versatile process for the production of these ketones in good yields and without expensive reactants.

According to the invention, this has been accomplished by the process of claim 1.

It has been found that secondary alcohols of the formula

$$R^{1'}–CHOH–R^{2'} \qquad (II)$$

in which $R^{1'}$ and $R^{2'}$ either have the same meaning as R^1 and R^2 above or, if R^1 and R^2 together are $–(CH_2)_m–[C(=O)]_n–(CH_2)_p–$ (i.e., if the product is a alicyclic diketone), are together $–(CH_2)_m–(CHOH)_n–(CH_2)_p–$ wherein m, n and p are as defined above, can smoothly be oxidized by peroxy compounds in the presence of a carboxylic acid and a manganese(IV) complex of 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) to give the corresponding ketones (I) in good to excellent yields.

Preferred peroxy compounds are hydrogen peroxide and peroxycarboxylic acids and mixtures thereof. It should be noted that hydrogen peroxide reacts with carboxylic acids to give peroxycarboxylic acids in an equilibrium reaction.
It is also possible to use other peroxy compounds, for example, *tert*-butyl hydroperoxide.

The most preferred carboxylic acid is acetic acid.

The preferred manganese(IV) complex of Me_3tacn is the dinuclear complex $[(Me_3tacn)_2Mn_2O_3]^{2+}[PF6]_2^-$ with three bridging oxo ligands [= tri-μ-oxobis(1,4,7-trimethyl-1,4,7-triazacyclononane)dimanganese bis(hexafluorophosphate)] which has been described by K. Wieghardt et al., *J. Am. Chem. Soc.* **1988**, *110*, 7398.

The process according to the invention may be carried out in polar aprotic solvents such as acetonitrile, nitromethane or mixtures thereof, acetonitrile being especially preferred.

A particularly preferred application of the process of this invention is the production of 1,4-cyclohexanedione (I; R^1,R^2 = $–(CH_2)_m–[C(=O)]_n–(CH_2)_p–$, $m = p = 2$, $n = 1$) from

1,4-cyclohexanediol (II; $R^{1'},R^{2'} = -(CH_2)_m-(CHOH)_n-(CH_2)_p-$, $m = p = 2$, $n = 1$) which is easily available from hydroquinone.

The process of the invention may be carried out at or near room temperature, e. g., at 0–40 °C, the reaction times being typically a few hours or less. The work-up can be done according to methods well known in the art, preferably after addition of a suitable reducing agent to destroy any excess of peroxy compound in order to avoid further oxidation and potential explosion hazards.

The invention is illustrated by the following non-limiting examples.

Example 1

Preparation of 1,4-Cyclohexanedione

To a solution of 0.5 g of 1,4-cyclohexanediol in 10 ml of acetonitrile were added 0.2 ml of a 6.32 mM acetonitrile solution of $[(Me_3tacn)_2Mn_2O_3][PF_6]_2$ and 0.4 ml of acetic acid (99%). A mixture of 2 ml of a 35% aqueous hydrogen peroxide solution in 11 ml of acetonitrile was added dropwise under vigorous stirring at 23 °C within one hour. After the addition the clear solution was stirred for additional 30 minutes, all volatiles removed in vacuo and the residue analysed by gas chromatography, ^1H- and ^{13}C NMR spectroscopy, showing >99% conversion and >99% selectivity. The analyses were compared with a commercially available (Fluka) sample of 1,4-cyclohexanedione.

Examples 2–9

In a procedure similar to that of example 1, several secondary alcohols were oxidized. In each case, a reaction mixture containing 0.23 M (1 M = 1 mol/l) of the respective alcohol, 1.0 M of hydrogen peroxide, 0.4×10^{-4} M of $[(Me_3tacn)_2Mn_2O_3][PF_6]_2$ and 0.5 M of acetic acid in acetonitrile as solvent was reacted at 20 °C for 3 h. The yields of the products were measured by gas chromatography after treatment of the samples with triphenylphosphine. The results are given in Table 1. All yields are based on the initial amounts of alcohol.

Table 1

Example	Alcohol	Conversion [%]	Product	Yield [%]
2	2-propanol	100	acetone	98
3	2-butanol	100	2-butanone	98
4	2-pentanol	99	2-pentanone	97
5	3-pentanol	98	3-pentanone	97
6	3-methyl-2-butanol	100	3-methyl-2-pentanone	100
7	3-hexanol	97	3-hexanone	96
8	cyclohexanol	95	cyclohexanone	91
9	1-phenylethanol	≈100	acetophenone	≈100

Claims

1. A process for the production of aliphatic or alicyclic monoketones or alicyclic diketones of the formula

$$R^1\text{–C(=O)–}R^2 \qquad \text{(I)}$$

in which R^1 is a linear or branched C_{1-10}-alkyl group, R^2 is a linear or branched C_{1-10}-alkyl group or a phenyl group,
or R^1 and R^2 together are $–(CH_2)_m–[C(=O)]_n–(CH_2)_p–$, wherein m and p independently are integers from 1 to 4 and n is 0 or 1, thus forming an alicyclic ring together with the carbonyl group of (I),
by oxidizing a secondary alcohol of formula

$$R^{1'}\text{–CHOH–}R^{2'} \qquad \text{(II)}$$

in which $R^{1'}$ and $R^{2'}$ either have the same meaning as R^1 and R^2 above or, if R^1 and R^2 together are $–(CH_2)_m–[C(=O)]_n–(CH_2)_p–$, are together $–(CH_2)_m–(CHOH)_n–(CH_2)_p–$ wherein m, n and p are as defined above,
with a peroxy compound in the presence of a carboxylic acid and a manganese(IV) complex of 1,4,7-trimethyl-1,4,7-triazacyclononane.

2. The process of claim 1 wherein the peroxy compound is selected from the group consisting of hydrogen peroxide and peroxycarboxylic acids and mixtures thereof.

3. The process of claim 1 or 2 wherein the carboxylic acid is acetic acid.

4. The process of any one of claims 1 to 3 wherein the manganese(IV) complex of 1,4,7-trimethyl-1,4,7-triazacyclononane is tri-μ-oxobis(1,4,7-trimethyl-1,4,7-triazacyclononane)-dimanganese bis(hexafluorophosphate).

5. The process of any one of claims 1 to 4 wherein the oxidation is conducted in a solvent selected from the group consisting of acetonitrile, nitromethane, and mixtures thereof.

6. The process of any one of claims 1 to 5 wherein R^1 and R^2 together are $-(CH_2)_2-C(=O)-(CH_2)_2-$ and $R^{1'}$ and $R^{2'}$ together are $-(CH_2)_2-CHOH-(CH_2)_2-$.

INTERNATIONAL SEARCH REPORT

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IPC 7 C07C45/29

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 100 24 617 A (BASF AG) 28 December 2000 (2000-12-28) the whole document -----	1,2,4-6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 10024617 A	28-12-2000	DE 19923121 A1 DE 10024617 A1	23-11-2000 28-12-2000