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(54) Titre : METHODE DE PREPARATION DE 1-CYCLOPROPYLETHAN-1-ONE
(54) Title: PROCESS FOR THE PRODUCTION OF CYCLOPROPYLMETHYLKETONE

(57) Abrégé/Abstract:

A process is described for the production of the known intermediate cyclopropylmethylketone which delivers a high yield, few side products, high reaction efficiency and turnover, and is more viable practically and commercially. In the presence of an excess of a Periodic Table Group I or Group II metal halide or quaternary phosphonium halide, α-acetyl-γ-butyrolactone is led continuously into a reaction vessel at 170-200 °C and cyclopropylmethylketone distilled off continuously. The halide is recovered and recycled in the process.

PF/5-18838/A

Process for the production of cyclopropylmethylketone

Abstract

A process is described for the production of the known intermediate cyclopropylmethylketone which delivers a high yield, few side products, high reaction efficiency and turnover, and is more viable practically and commercially. In the presence of an excess of a Periodic Table Group I or Group II metal halide or quaternary phosphonium halide, α-acetyl-γ-butyrolactone is led continuously into a reaction vessel at 170-200 °C and cyclopropylmethylketone distilled off continuously. The halide is recovered and recycled in the process.

CLAIMS

1. A process for the production of cyclopropylmethylketone by heating from 160 °C to 220 °C α-acetyl-γ-butyrolactone in the presence of a halide, optionally in an inert solvent, characterized in that i) the halide is selected from the group of LiCl and MX_n, wherein M is $Li^\oplus$, $Na^\oplus$, $K^\oplus$ or quaternary phosphonium when n=1, and $Mg^{2\oplus}$ or $Ca^{2\oplus}$ when n=2, and X is $Br^\ominus$ or $I^\ominus$, ii) the said acetylbutyrolactone is added throughout the reaction continuously and simultaneously cyclopropylmethylketone is distilled off continuously, and iii) a large excess of the halide is maintained from the start to the end of the reaction.

2. A process according to claim 1, characterized in that the halide is the bromide or iodide of Na.

3. A process according to claim 1, characterized in that the halide is CaI_2.

4. A process according to claim 1, characterized in that the quaternary phosphonium halide corresponds to the formula $R_1R_2R_3R_4P^\oplus X^\ominus$ wherein R_1,R_2,$R_3$and R_4 represent independently linear or branched C_1-C_{20} alkyl, cyclo alkyl of 5-8 ring carbons, phenyl or benzyl, whereby the cyclic residues are unsubstituted or substituted with C_1-C_9-alkyl or C_1-C_9-alkoxy, and X is $Br^\ominus$ or $I^\ominus$.

5. A process according to claim 4, wherein the cyclic residues are unsubstituted or substituted with C_1-C_6-alkyl or C_1-C_6-alkoxy.

6. A process according to claim 4, wherein R_1,R_2,R_3 and R_4 represent independently C_1-C_{12}-alkyl.

7. A process according to claim 1, characterized in that the halide is essentially dissolved in the inert solvent.

8. A process according to claim 1, characterized in that the halide concentration in the solvent is between 1 and 40 volume-%.

9. A process according to claim 1, characterized in that the halide concentration in the solvent is between 2 and 30 volume-%.

10. A process according to claim 1, characterized in that the halide concentration in the solvent is between 5 and 25 volume-%.

11. A process according to claim 10, characterized in that the halide concentration in the solvent is between 10 and 20 volume-%.

12. A process according to claim 1, characterized in that the halide is present in an excess of 1 to 100 molar equivalents of acetylbutyrolactone at any moment during the reaction.

13. A process according to claim 12 where the excess is from 2 to 50 molar equivalents.

14. A process according to claim 12 where the excess is from 3 to 10 molar equivalents.

15. A process according to claim 1 where the inert solvent is aprotic.

16. A process according to claim 1, characterized in that the boiling temperature of the solvent exceeds the reaction temperature by more than 20 °C.

17. A process according to claim 1 wherein the boiling point of the solvent exceeds the reaction temperature by more than 40 °C.

18. A process according to claim 15 where the solvent is tetramethylenesulfone, dimethylethylurea, dimethylpropylurea, N-methylpyrrolidone, polyethylglycolether or tetrahydronaphthalene.

19. A process according to claim 1, characterized in that the temperature range for the reaction is 160 °C - 210 °C.

20. A process according to claim 17, characterized in that the temperature range for the reaction is 170 °C - 200 °C.

21. A process according to claim 1, characterized in that the reaction is carried out at atmospheric pressure.

22. A process according to claim 1, characterized in that the halide is recycled.

23. A process according to claim 22, characterized in that in recycling the halide the solvent is distilled off, water is added thereby forming an aqueous halide solution, an organic residue is removed by extraction, the solvent is re-added to the aqueous halide solution, the water is distilled off and the reaction is started again.

24. A process according to claim 1, characterized in that the continuous process is carried out in a reaction vessel.

25. A process according to claim 1, characterized in that the continuous process is carried out on a thin film evaporator.

26. A process according to claim 1, characterized in that a distillation column consisting of a number of plates is connected to the reaction vessel, a temperature gradient forms within said column and cyclopropylmethylketone of improved quality is collected at the plate number(s) corresponding to its boiling point range.

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