

EXAMPLE I**A) Preparation of the formate of 1,5-dimethylbicyclo-[3.2.1] octanol-8**

An amount of 420 ml (11.46 mol.) 98-100% formic acid was introduced into a round-bottom flask and, with vigorous stirring, 430 ml (2.74 mol.) dimethyl-1,5-cyclo-octadiene (a mixture of 80%w

5 1,5-dimethyl-1,5-cyclo-octadiene and 20%w 1,6-dimethyl-1,5-cyclo-octadiene) were pumped into the formic acid at a temperature of 60°C over a period of 1.5 h. The conversion of the dimethylcyclo-octadiene was complete. Then, 90% of the formic acid was distilled off in vacuum at 60°C, upon which a bicyclic olefin, too, distilled over, which was isolated by extraction with pentane. The residue was taken up in 200 ml pentane and washed with water and an aqueous solution of NaHCO₃. After being dried over Na₂SO₄ the pentane was
10 distilled off and the residue was subjected to fractional distillation in vacuum. The yield of the formate of 1,5-dimethylbicyclo [3.2.1] octanol-8, boiling point 68°C at 133 Pa, was 392 g (2.15 mol.; 97% calculated on 1,5-dimethyl-1,5-cyclo-octadiene). By means of gas chromatography the purity was shown to be higher than 99%. The product was identified by measurement of the infra-red spectrum and the NMR spectrum. Infra-red spectrum: 1000, 1185 and 1730 cm⁻¹. The formate consisted of 92%w syn- and of 8%w anti-isomer.

15 When the experiment was repeated with formic acid containing 10%w water, the formate yield was 94.8% calculated on 1,5-dimethyl-1,5-cyclo-octadiene. Further, the use of formic acid with an even higher water content (40%w) was found to require addition of a phase transfer catalyst (ALIQAT) to give reasonable yields.

B) Preparation of 1,5-dimethylbicyclo [3.2.1] - octanol-8**1) by hydrolysis**

20 An amount of 182 g of the formate of 1,5-dimethyl-bicyclo [3.2.1] octanol-8 was dissolved in 100 ml methanol and the solution was slowly added to a mixture of 50 g NaOH, 50 ml H₂O and 200 ml methanol. After the exothermal reaction was finished, the product was refluxed for 10 minutes. The methanol was distilled off in vacuum and pentane was added to the residue. After washing with water and drying over
25 Na₂SO₄ 152 g crystalline 1,5-dimethylbicyclo- [3.2.1] octanol-8 (melting point 43°C) was obtained in quantitative yield by concentrating and cooling the pentane solution. The structure was confirmed by measuring the infra-red and NMR spectra. The weights of syn- and anti-isomer were in the ratio of 92:8.

2) by alcoholysis

30 An amount of 8.8 g of the formate of 1,5-dimethylbicyclo [3.2.1] octanol-8 was dissolved in 50 ml absolute methanol and 10 mg sodium were added to the solution. After refluxing for four hours methanol and the methyl formate formed were distilled off and the residue was taken up into pentane. The solution was washed with water and dried over Na₂SO₄. Distilling off the pentane yielded 6 g of crystalline product with a purity higher than 98%.

EXAMPLE II**A) Preparation of the acetate of 1,5-dimethylbicyclo-[3.2.1] octanol-8**

35 a) An amount of 20.4 g dimethyl-1,5-cyclo-octadiene (a mixture of 80%w 1,5-dimethyl-1,5-cyclo-octadiene and 20%w 1,6-dimethyl-1,5-cyclo-octadiene) was dissolved in 100 ml acetic acid and, after addition of 2 g "AMBERLYST" 15 ("Amberlyst" is a Registered Trade Mark), was refluxed with vigorous stirring. After six
40 hours the conversion was 98%. The reaction mixture was filtered, diluted with water and extracted with pentane. The pentane solution was washed with water and with an aqueous NaHCO₃ solution, dried, evaporated and fractionally distilled. The yield of the desired acetate was 53.3%. The weights of syn and anti-isomer were in the ratio of 85:15.

45 b) An amount of 13.6 g (0.1 mol.) dimethyl-1,5-cyclo-octadiene (a mixture of 80%w 1,5-dimethyl-1,5-cyclo-octadiene and 20%w 1,6-dimethyl-1,5-cyclo-octadiene) was dissolved in 60 ml acetic acid. The solution was cooled to 12°C and 0.5 ml H₂SO₄ was added dropwise with vigorous stirring. While this was being done the temperature increased to 39°C. After another two hours at room temperature the conversion of the dimethylcyclo-octadiene was 98% and the reaction mixture was worked up in the way described under a). The yield of the desired acetate was 24%. The weights of syn- and anti-isomer were
50 in the ratio of 85:15.

B) Preparation of 1,5-dimethylbicyclo [3.2.1] - octanol-8

55 A solution of 13.2 g KOH in 10 ml water and 90 ml methanol was added to a solution of 19.6 g of the acetate of 1,5-dimethylbicyclo [3.2.1] octanol-8 in 50 ml methanol. The mixture was refluxed for two hours. The methanol was then distilled off and water and pentane were added to the residue. The pentane layer was washed with water and dried over Na₂SO₄. Concentration of the pentane solution gave a crystalline product with a melting point of 43°C. The yield was quantitative.

EXAMPLE III

60 An amount of 136 g dimethyl-1,5-cyclo-octadiene (a mixture of 80%w 1,5-dimethyl-1,5-cyclo-octadiene and 20%w 1,6-dimethyl-1,5-cyclo-octadiene) was added over a period of 30 minutes with stirring to 178 g trichloroacetic acid to form 1,5-dimethylbicyclo [3.2.1] octan-8-yl trichloroacetate. (Infra-red spectrum at 3.44, 3.53, 5.73, 6.94, 7.32, 8.08, 8.92, 9.12, 9.50, 9.98, 10.30, 10.70, 11.60, 11.90, 12.20, 12.92, 13.35 and 14.85 microns). Care was taken, by means of cooling with ice, that the temperature remained below 25°C. The ice bath was then removed and the stirring continued for another three hours, during which the temperature
65 increased to 29°C. A solution of 55 g NaOH in 200 ml water was slowly added to the reaction mixture with

SPECIFICATION

A process for the preparation of 1,5-dimethyl-bicyclo [3.2.1] octanol-8

5 The invention relates to a new process for the preparation of 1,5-dimethylbicyclo [3.2.1] octanol-8 and with the alcohol so prepared. 5

1,5-Dimethylbicyclo [3.2.1] octanol-8 is a known compound with a high thermal stability and therefore, as has been mentioned in U.K. patent application 11,586/77, is a suitable starting material for the preparation of additives for lubricating oil. The said compound may further be used as a base material for the preparation of 10 aroma chemicals. 10

It is stated by J.K. Whitesell, R.S. Matthews and P.A. SOLOMON, Tetrahedron Letters No. 19, pp. 1549-1552, 1976, that 1,5-dimethylbicyclo [3.2.1] octanol-8 can be obtained in a yield of 50% by reacting 1,5-dimethyl-1,5-cyclo-octadiene with a solution of perchloric acid in a mixture of water and dioxane. However, the handling of perchloric acid has practical drawbacks.

15 According to the invention, a process for preparing 1,5-dimethylbicyclo [3.2.1] octanol-8 comprises reacting 1,5-dimethyl-1,5-cyclo-octadiene, optionally in the presence of an acidic catalyst, with a carboxylic acid of formula RCOOH, wherein R represents hydrogen or a substituted or non-substituted hydrocarbon group, to form an ester of 1,5-dimethyl-bicyclo[3.2.1] octanol-8, and hydrolyzing or alcoholizing the ester so 15 formed to obtain 1,5-dimethylbicyclo [3.2.1] octanol-8.

20 If the pK-value of the acid RCOOH is less than four, the reaction can be performed in the absence of a catalyst. Very good results are obtained with formic acid. Other suitable carboxylic acids with a pK-value less than four are, for instance, aliphatic, cycloaliphatic and aromatic carboxylic acids, with, preferably, not more than eight carbon atoms which are substituted with one or more halogen atoms or carboxyl, hydroxyl, cyano or nitro groups. Aliphatic carboxylic acids with from two to five carbon atoms which are substituted with one 25 or more halogen atoms, such as e.g. mono-, di-, and trifluoroacetic acid and mono-, di- and trichloroacetic acid are preferred. Examples of other suitable carboxylic acids with a pK-value less than four are oxalic acid, cyanobutyric acid, chlorobenzoic acid, phthalic acid, nitrobenzoic acid and hydroxybenzoic acid. 25

Carboxylic acids with a pK-value greater than four, such as the aliphatic carboxylic acids with two or more carbon atoms do not generally react with 1,5-dimethyl-1,5-cyclo-octadiene. However, these acids, preferably 30 aliphatic carboxylic acids with from two to eight, in particular from two to five carbon atoms, can be used in the presence of an acid catalyst, such as for instance sulphuric acid, phosphoric acid, p-toluenesulphonic acid or, preferably, an acidic ion-exchange resin, such as for instance the strongly acidic macroreticular cation-exchange resin "AMBERLYST" 15 (BDH Chemicals Ltd.). The word "Amberlyst" is a Registered Trade 30 Mark.

35 The reaction of the 1,5-dimethyl-1,5-cyclo-octadiene with the acid RCOOH is generally carried out at temperatures between 0°C and 150°C. If desired, a solvent as for instance CH₂Cl₂, CHCl₃, CCl₄, benzene, toluene, xylene or nitromethane may be added. 35

Particularly good results are obtained by heating 1,5-dimethyl-1,5-cyclo-octadiene with formic acid at a temperature of from 40 to 100°C. It is preferred to use an excess of formic acid, for instance 2 to 10 mol. per 40 mol. dimethylcyclo-octadiene. The excess of formic acid may be distilled off after the reaction and the residue be hydrolyzed or alcoholized. If desired, the formate of 1,5-dimethylbicyclo [3.2.1] octanol-8 may first be isolated by working up the residue in the usual way, but this is not necessary. 40

Although it is preferred to use formic acid with a water content of from 0 to 10%w, it is possible, if necessary, to use formic acid with a higher water content of from 10 to 40%w, in particular if a phase transfer catalyst, 45 such as for instance ALIQUAT (tri-sec. octyl-methylammonium chloride) ("ALIQUAT" is a registered trade mark) is added to the reaction mixture. 45

Since both the preparation of the formate and the hydrolysis or alcoholysis of the ester formed proceed virtually quantitatively, a much higher yield of 1,5-dimethylbicyclo [3.2.1] octanol-8 can be obtained with the process according to the invention than with the known process.

50 A suitable starting material in the new process is a mixture consisting of 1,5- and 1,6-dimethyl-1,5-cyclo-octadiene, which, according to French patent specification 1,283,217 and Netherlands patent application 7800529, can be obtained by dimerization of isoprene. The presence of 1,6-dimethyl-1,5-cyclo-octadiene in the reaction mixture does not interfere with the formation of the desired ester or its separation from the reaction mixture. 50

55 The hydrolysis or alcoholysis of the ester of 1,5-dimethylbicyclo [3.2.1] octanol-8 can be carried out by any known method. The hydrolysis may, for instance, be carried out by refluxing the ester with an aqueous solution of an acid or a base. Good results can, for instance, be obtained by boiling the ester with a solution of a hydroxide of an alkali or alkaline-earth metal, in a mixture of water and an alcohol, for instance methanol or ethanol. The alcoholysis may, for instance, be effected by boiling the ester with a solution of an alcoholate 60 of an alkali metal or alkaline-earth metal in an absolute alcohol, such as for instance methanol or ethanol. 60

The esters of 1,5-dimethylbicyclo [3.2.1]-octanol-8 with the carboxylic acid RCOOH which are obtained as intermediate products in the process according to the invention, which are novel compounds, are included within the subject matter of our co-pending UK Patent Application No. 7916210.

The invention will now be illustrated with reference to the following Examples.

stirring. The temperature was kept below 20°C by means of cooling with ice. The mixture obtained was extracted with cyclohexane and the extract was dried over MgSO₄. When the solvent was distilled off a residue of 148 g was obtained which contained 54%w 1,5-dimethylbicyclo [3.2.1] octanol-8.

5 EXAMPLE IV

An amount of 11.4 g trifluoroacetic acid was slowly added, with stirring, to an ice-cooled solution of 13.6 g dimethyl-1,5-cyclo-octadiene (a mixture of 80%w 1,5-dimethyl-1,5-cyclo-octadiene and 20%w 1,6-dimethyl-1,5-cyclo-octadiene) in 50 g dichloromethane over a period of 35 minutes. The ice was then removed and the reaction mixture, after it had reached room temperature, was washed with an aqueous solution of NaHCO₃. Drying over MgSO₄ and evaporating the reaction mixture yielded 21.2 g residue consisting mainly of 1,5-dimethylbicyclo [3.2.1] octan-8-yl trifluoro-acetate. (Infra-red spectrum at 3.44, 3.51, 5.67, 6.95, 7.40, 7.50, 8.30, 8.70, 9.14, 10.13, 10.27, 10.50, 13.04, 13.66 and 14.13 microns). A solution of 4 g NaOH in 10 ml water and 5 ml CH₃OH were added to 5 g of this residue, during which the temperature increased to 30°C. Working up of the reaction mixture in the usual way after three hours yielded 3.45 g residue consisting of 1,5-dimethylbicyclo [3.2.1] octanol-8. Infra-red spectrum: 1045; 1100; 1430; 2800 and 2840 cm⁻¹.

CLAIMS

1. A process for the preparation of 1,5-dimethylbicyclo[3.2.1]-octanol-8, characterized in that 1,5-dimethyl-1,5-cyclo-octadiene is reacted with a carboxylic acid of formula RCOOH, wherein R represents hydrogen or a substituted or non-substituted hydrocarbon group, to form an ester of 1,5-dimethylbicyclo[3.2.1]octanol-8 and hydrolyzing or alcoholyzing the ester so formed to obtain 1,5-dimethylbicyclo[3.2.1]octanol-8.
2. A process according to claim 1, characterized in that the reaction with said carboxylic acid of formula RCOOH is carried out in the presence of an acidic catalyst.
3. A process according to claim 1 or claim 2, characterized in that the carboxylic acid is an aliphatic carboxylic acid with from two to five carbon atoms substituted with one or more halogen atoms.
4. A process according to claim 2, characterized in that the carboxylic acid is an unsubstituted aliphatic carboxylic acid with from two to eight carbon atoms and the reaction is carried out in the presence of an acidic ion exchange resin.
5. A process according to any one of claims 1-4, characterized in that the reaction of 1,5-dimethyl-1,5-cyclo-octadiene with the carboxylic acid RCOOH is carried out at a temperature between 0 and 150°C.
6. A process according to claim 1 or claim 2, characterized in that 1,5-dimethyl-1,5-cyclo-octadiene is heated with formic acid at a temperature of from 40°C to 100°C.
7. A process according to any one of claims 1, 2 or 6, characterized in that 2 to 10 mol. formic acid are used per mol. 1,5-dimethyl-1,5-cyclo-octadiene.
8. A process according to any one of claims 1, 2, 6 or 7, characterized in that formic acid with a water content of from 0 to 10% w is used.
9. A process according to any one of claims 1, 2, 6 or 7, characterized in that formic acid with a water content of from 10 to 40%w in the presence of a phase transfer catalyst is used.
10. A process according to any one of claims 1-9, characterized in that a mixture consisting of 1,5- and 1,6-dimethyl-1,5-cyclo-octadiene which has been obtained by dimerization of isoprene, is used as the starting material.
11. A process as claimed in claim 1 or claim 2, substantially as hereinbefore described with particular reference to any one of Examples I to IV.
12. 1,5-Dimethylbicyclo[3.2.1]octanol-8 whenever prepared by a process as claimed in any one of claims 1 to 11.



stirring. The temperature was kept below 20°C by means of cooling with ice. The mixture obtained was extracted with cyclohexane and the extract was dried over MgSO₄. When the solvent was distilled off a residue of 148 g was obtained which contained 54%w 1,5-dimethylbicyclo [3.2.1] octanol-8.

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- 25 2. A process according to claim 1, characterized in that the reaction with said carboxylic acid of formula RCOOH is carried out in the presence of an acidic catalyst. 25
3. A process according to claim 1 or claim 2, characterized in that the carboxylic acid is an aliphatic carboxylic acid with from two to five carbon atoms substituted with one or more halogen atoms.
4. A process according to claim 2, characterized in that the carboxylic acid is an unsubstituted aliphatic
30 carboxylic acid with from two to eight carbon atoms and the reaction is carried out in the presence of an acidic ion exchange resin. 30
5. A process according to any one of claims 1-4, characterized in that the reaction of 1,5-dimethyl-1,5-cyclo-octadiene with the carboxylic acid RCOOH is carried out at a temperature between 0 and 150°C.
- 35 6. A process according to claim 1 or claim 2, characterized in that 1,5-dimethyl-1,5-cyclo-octadiene is heated with formic acid at a temperature of from 40°C to 100°C. 35
7. A process according to any one of claims 1, 2 or 6, characterized in that 2 to 10 mol. formic acid are used per mol. 1,5-dimethyl-1,5-cyclo-octadiene.
8. A process according to any one of claims 1, 2, 6 or 7, characterized in that formic acid with a water
40 content of from 0 to 10% w is used. 40
9. A process according to any one of claims 1, 2, 6 or 7, characterized in that formic acid with a water content of from 10 to 40%w in the presence of a phase transfer catalyst is used.
10. A process according to any one of claims 1-9, characterized in that a mixture consisting of 1,5- and 1,6-dimethyl-1,5-cyclo-octadiene which has been obtained by dimerization of isoprene, is used as the
45 starting material. 45
11. A process as claimed in claim 1 or claim 2, substantially as hereinbefore described with particular reference to any one of Examples I to IV.
12. 1,5-Dimethylbicyclo[3.2.1]octanol-8 whenever prepared by a process as claimed in any one of claims 1 to 11.