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PROCESS FOR PREPARING 2,13-TETRADECANEDIONE FROM 1-METHYLCYCLOHEXYL HYDROPEROXIDE

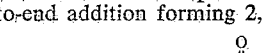
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This invention relates to reactions of organic peroxides, and more particularly to a process for preparing 2,13-tetradecanedione by decomposition of 1-methylcyclohexyl hydroperoxide in the presence of a ferrous salt.

In 1946, N. A. Milas postulated that, in the pyrolysis of tertiary butyl 1-methylcyclohexyl 1-peroxide, in the vapor phase, a 1-methylcyclohexyl-1-oxy radical, which was capable of undergoing ring opening, was produced (Journal of the American Chemical Society, 68, 1938–40 (1946)). Quite recently Hawkins et al. (cf. Journal of the Chemical Society (London), 1950, 2805; USP 2,575,014, Br. 655,118, Fr. 983,799; Chemical Abstracts, 45, 3354–5 (1951)) have reported that decomposition of 1-methylcyclohexyl hydroperoxide produced the same radical which thereupon underwent ring opening and end-to-end addition forming 2,13-tetradecanedione,



In the Hawkins et al. process, it was essential that an aqueous solution of ferrous salt be present in the reaction mixture at the time when the reaction which produced the diketone was taking place. The Hawkins et al. reaction mixture comprised two liquid phases.

The present applicant has discovered that while the Hawkins process gives good yields of diketone from 1-methylcyclopentyl hydroperoxide there is a serious disadvantage in carrying out the synthesis of 2,13-tetradecanedione from 1-methylcyclohexyl hydroperoxide in this manner. In particular, the yields of 2,13-tetradecanedione in such two-phase systems are quite low, namely about 10% of the theoretical. For such a process to be of value in the manufacture of relatively low cost difunctional organic compounds (i. e. sebacic acid or other nylon intermediates) it obviously was necessary that very much higher yields be realized.

An object of this invention is to obtain an improved yield of 2,13-tetradecanedione from 1-methylcyclohexyl hydroperoxide.

It has been discovered, in accordance with this invention, that the coupling of 1-methylcyclohexyl hydroperoxide in a homogeneous reaction mixture preferably at temperatures within the range of −50° C. to +100° C. containing an inert organic solvent and a ferrous salt which is soluble in the said solvent gives yields of 2,13-tetradecanedione several times as high as the yields obtained by the heretofore known process. Thus, in accordance with this invention, it has been found that it is not necessary to employ an aqueous solution containing ferrous ion during the time when the formation of the diketone is taking place, and that a surprising increase in yield and reaction rate is achieved by the use of a homogeneous non-aqueous reaction system at relatively low temperatures.

In carrying out the process of this invention it is preferable to employ an organic solvent such as benzene, cyclohexane, methylcyclohexane, etc., e. g., one which is inert under the coupling conditions. The preferred organic medium is methylcyclohexane because it is convenient to prepare methylcyclohexyl hydroperoxide by reaction between oxygen and methylcyclohexane, thus producing a suitable solution for conversion to diketone by the process of this invention.

Any ferrous compound which is soluble in the reaction mixture may be employed. When a hydrocarbon diluent is present, suitable ferrous compounds include ferrous salts of the relatively long chain alkanoic acids, e. g. ferrous caproate, ferrous heptanoate, ferrous oleate, ferrous stearate, etc.

In one of the preferred embodiments of the invention the crude reaction product containing 2,13-tetradecanedione is extracted with water containing an amount of aqueous acid stoichiometrically sufficient to remove the iron from the non-aqueous phase to the aqueous phase. The acid used should be one which forms a ferric salt which is more soluble in the aqueous phase than in the non-aqueous phase. Suitable acids are sulfuric, phosphoric, formic, hydroxyacetic, oxalic, etc. Any acid capable of displacing the anionic radical of the ferric salt can be used. When the ferric salt is a salt of a long chain alkanoic acid, the alkanoic acid is liberated, and remains in the non-aqueous phase. It can be separated by distillation, but it is preferred to convert it to the sodium salt by reaction with sodium hydroxide. The aqueous ferric iron can be very readily reduced to ferrous iron by means of hydrogen, whereupon it can be extracted from the aqueous medium to the non-aqueous medium upon reaction with the sodium alkanoate, obtained as above described. The net result of these operations is the recovery of the ferrous salt from ferric salt in the non-aqueous phase, with the formation of sodium sulfate or other such sodium salt which can be discarded.

The process of the invention can be illustrated further by means of the following examples.

Example 1.—A solution of ferrous heptanoate in benzene was prepared as follows: To a mixture of 15.6 g. (0.12 mole) of heptanoic acid and 100 ml. of water was added 4.0 g. (0.10 mole) of sodium hydroxide in the form of a 10% aqueous solution. About 100 ml. of benzene was added, and a stream of nitrogen gas was bubbled through the mixture to protect it from air oxidation. The mixture was stirred while 13.9 g. (0.05 mole) of ferrous sulfate heptahydrate was added. As the solid ferrous salt dissolved, it reacted to form ferrous heptanoate which was preferentially extracted into the benzene layer. Stirring was stopped, and the benzene layer was separated from the aqueous layer. Analysis indicated that the benzene layer contained the major part of the ferrous ion.

To about 100 ml. of a benzene solution containing 46.2 milliequivalents of ferrous ion as ferrous heptanoate was added 4.23 g. of 1-methylcyclohexyl hydroperoxide. The mixture remained homogeneous at all times. The temperature of the reaction mixture rose from 25° C. to 35° C. immediately after the addition of the hydroperoxide, and the reaction appeared to be over within a few minutes.

When the reaction was over, the mixture was treated with 12 g. of sodium hydroxide in the form of a 10% aqueous solution. This caused the iron to be precipitated as ferrous and ferric hydroxides and removed the heptanoic acid to the aqueous layer as sodium heptanoate. The benzene layer was separated and distilled to give 1.98 g. (54% of theoretical) of 2,13-tetradecanedione.

Example 2.—Example 1 was repeated using a solution of 1-methylcyclohexyl hydroperoxide in 100 ml. of benzene instead of the pure hydroperoxide. In this case the ferrous heptanoate solution was added to the hydroperoxide solution. The yield of 2,13-tetradecanedione was 53% of theoretical.

Example 3.—Example 1 was repeated using a solution of ferrous heptanoate in methylcyclohexane instead of benzene. The yield of 2,13-tetradecanedione was 40% of theoretical.

Example 4.—Example 1 was repeated except that the iron compounds were removed from the reaction mixture by extraction with dilute sulfuric acid. The benzene layer was then extracted with 10% aqueous sodium carbonate to remove heptanoic acid. Distillation of the benzene layer gave the same result as in Example 1.

Example 5.—Air was injected through a sparger into 500 ml. of methylcyclohexane at a temperature of 125° C. under a pressure of 100–200 lbs./sq. in. The effluent gas was vented through a valve at the top of the vessel

at the rate of 50 liters/hr. (S. T. P.). When the analysis of the reaction mixture indicated about 3% peroxide (calculated as 1-methylcyclohexyl hydroperoxide), methylcyclohexane was injected into the reaction vessel at a rate sufficient to hold the peroxide content approximately constant. Liquid was continuously withdrawn from the oxidation vessel at a rate equal to the methylcyclohexane addition.

A 3686 ml. portion of oxidized methylcyclohexane produced in the above manner was passed through a vertical column containing four pounds of activated alumina. The effluent methylcyclohexane at the bottom of the column contained no hydroperoxide or other oxygenated material. It was returned to the oxidation vessel for further oxidation. To the column of alumina was then added about 2 liters of methanol. The first 750 ml. of effluent methanol contained 58.3 g. of hydroperoxide calculated as 1-methylcyclohexyl hydroperoxide, and continued elution with methanol resulted in further recovery of smaller amounts of hydroperoxide. In all, the hydroperoxide recovery was over 90%.

A 50 ml. portion of a methanolic solution, prepared as above described and containing 3.64 g. of crude hydroperoxide, was added rapidly to 11.7 grams of ferrous sulfate heptahydrate in 120 ml. of methanol. There was an immediate temperature rise from 23° to 35° C. indicating rapid reaction. The reaction mixture remained completely homogeneous. The mixture was boiled down to a thick paste and 75 ml. water was added. Extraction of the mixture with ether followed by distillation of the ether gave 1.58 grams (50% of theoretical) of crude crystalline 2,13-tetradecanedione.

Example 6.—A solution of about 3 to 5% 1-methylcyclohexyl hydroperoxide in methylcyclohexane is prepared by oxidation as described in Example 5. This solution is added rapidly to a solution of ferrous heptanoate in methylcyclohexane such that the molar ratio of ferrous heptanoate to the hydroperoxide is 1.0 to 1.5. Reaction occurs at room temperature to give 2,13-tetradecanedione. Extraction of resulting mixture with an equivalent quantity of dilute aqueous sulfuric acid causes the iron to transfer to the aqueous layer. Neutralization of the heptanoic acid in the methylcyclohexane layer with aqueous sodium hydroxide gives an aqueous layer of sodium heptanoate. Hydrogenation of the aqueous solution containing the iron salt in the presence of a palladium catalyst at atmospheric pressure and room temperature converts ferric iron to ferrous iron. Recovery of 2,13-tetradecanedione and methylcyclohexane from the non-aqueous reaction product is accomplished by distillation, and the recovered methylcyclohexane is made up to the quantity originally employed by adding a sufficient quantity of methylcyclohexane. The aqueous solution of sodium heptanoate, when admixed with a quantity of methylcyclohexane and the aqueous solution of ferrous salt from the hydrogenation operation, gives ferrous heptanoate, which transfers to the hydrocarbon phase. This phase is separated and is now ready for recycling and reaction with a further quantity of 1-methylcyclohexyl hydroperoxide as above described.

Example 7.—Example 5 was repeated, except that instead of an anhydrous methanol solution a methanol solution containing 50% by weight of water was used. The reaction mixture did not remain homogeneous and the yield of crude crystalline diketone was only 14% of the theoretical.

The foregoing examples are illustrative, and are not intended to limit the invention. Numerous modifications of the invention will occur to those who are skilled in the art. It is however, important that the presence of an aqueous phase during diketone-formation be avoided because the yield is more than doubled through avoidance of such a separate aqueous phase. In preparing a solution of ferrous salt in the organic reaction medium, an aqueous phase may of course be present. In this connection, it is advantageous to employ (in the manner described in Example 1) an acid which contains at least 6 carbon atoms. This is shown in the following table, which records the results obtained in a series of tests which were carried out as described in Example 1, except that methylcyclohexane was used in place of benzene as solvent. The same molar amounts (0.12 mol) of the acids specified in the table were used in place of heptanoic acid. The methylcyclohexane solutions thus obtained were analyzed for ferrous iron, with results as follows.

Table I.—Effect of chain length of alkanoic acid on distribution of ferrous iron between aqueous phase and hydrocarbon phase.

Acid	Concentration of ferrous iron (in milliequivalents per ml.)	Approximate percentage of ferrous iron in the hydrocarbon phase
Heptanoic	0.35	77
Caproic	0.078	17
Valeric	0.006	1.3

Since ease of transfer to the non-aqueous phase is an important characteristic of the ferrous salt, it is important, in accordance with the data given above, that the organic carboxylic acid contain at least six carbon atoms per molecule.

The 2,13-tetradecanedione which is obtained by the process of this invention is highly useful as an intermediate in the manufacture of sebacic acid. The conversion of 2,13-tetradecanedione to sebacic acid is accomplished by means of nitric acid oxidation at a temperature of about 60° to 85° C. The preferred concentration of nitric acid for use in the conversion of this diketone to sebacic acid is about 60%. The nitric acid solution contains 0.15% copper in the form of cupric nitrate and 0.05% ammonium metavanadate as catalysts. The oxides of nitrogen which are generated during the nitric acid oxidation can be reoxidized and reabsorbed in water, and recycled with 60% nitric acid. The crude nitric acid oxidation product can be worked up without serious difficulty by distilling the supply of excess nitric acid which is employed and returning it to the nitric acid feed followed by cooling the residue from about 100–250° C. to room temperature to produce crystallization of the sebacic acid. The crystallizer mother liquors can be recovered and fed back into the nitric acid oxidizer as desired. The quantity of sebacic acid obtainable in this manner is about 100 parts or more per 160 parts of 2,13-tetradecanedione introduced.

The conversion of 2,13-tetradecanedione to sebacic acid can also be achieved by other oxidation methods such as by air oxidation with or without an organic diluent such as acetic acid (cobalt, manganese, etc., compounds may be used as catalysts if desired). Oxidation with hypochlorites such as NaOCl gives dodecanedioic acid, a valuable intermediate for polyamide resins.

The 2,13-tetradecanedione obtained as hereinabove described is also of considerable value as an intermediate in the manufacture of 2,13-diaminotetradecane which can be obtained from the diketone by reductive amination. This diamine can be converted to a nylon type resin by forming a salt with sebacic acid or other alkanedioic acid followed by polymerization in the known manner.

I claim:

1. A process for preparing 2,13-tetradecanedione which comprises subjecting 1-methylcylcohexyl hydroperoxide in a homogene ous reaction mixture containing an inert organic diluent to the action of a ferrous salt of a long chain alkanoic acid in which the alkanoate radical contains from 6 to 18 carbon atoms.

2. Process of claim 1 wherein the organic diluent is methylcyclohexane.

3. Process of claim 2, in which the ferric iron produced during the formation of 2,13-tetradecanedione is thereafter catalytically hydrogenated to produce ferrous iron in an aqueous system and the ferrous iron upon reaction with sodium salt of said alkanoic acid to form ferrous alkanoate is transferred by extraction from the aqueous hydrogenation product to a methylcyclohexane layer, and thereafter the 1-methylcyclohexyl hydroperoxide is subjected to the action of the ferrous iron contained in the said layer.

4. Process of claim 3 wherein the said hydrogenation is carried out in the presence of a palladium-containing catalyst.

5. Process of claim 3 wherein the ferrous iron in the methylcyclohexane layer is in the form of ferrous heptanoate.

6. A process which comprises heating at a temperature

of −50° to +100° C. a methylcyclohexane-containing and 1-methylcyclohexyl hydroperoxide-containing air oxidation product of methylcyclohexane in a homogeneous anhydrous system with ferrous heptanoate in a reaction vessel wherein 1-methylcyclohexyl hydroperoxide is converted to 2,13-tetradecanedione, thereupon extracting ferric salt from the resulting reaction product with aqueous sulfuric acid, whereby heptanoic acid is liberated and remains in the methylcyclohexane layer, converting the said heptanoic acid to sodium heptanoate, separating 2,13-tetradecanedione from the methylcylohexane layer, hydrogenating the aqueous extract in the presence of a palladium catalyst to convert substantially all of the ferric sulfate to ferrous sulfate, reacting the said ferrous sulfate with sodium heptanoate to produce ferrous heptanoate and sodium sulfate, extracting ferrous heptanoate from the resulting mixture by means of methylcyclohexane, and returning the methylcyclohexane extract containing the ferrous heptanoate to the reaction vessel containing the 1-methylcyclohexyl hydroperoxide.

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