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CONDENSATION OF DIALKYL SUCCINATES

Paul-Otto Lenel, Norton-on-Tees, England, assignor to Imperial Chemical Industries Limited, London, England, a corporation of Great Britain

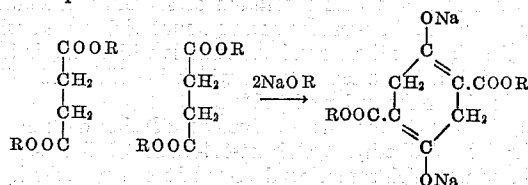
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This invention relates to the condensation of dialkyl succinates.

It is already known to condense dialkyl succinates to give derivatives of dialkyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylates. Thus, a dialkyl succinate, with a sodium alkoxide, gives rise to the di-sodium derivative of a dialkyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylate, according to the equation:



In reactions of this type, it has been proposed to employ, as condensing agent, sodium or potassium metal, used either alone or with a small amount of alcohol, sodium or potassium alkoxides, or sodium or potassium hydride.

In the processes hitherto disclosed for the production of di-alkali metal derivatives of dialkyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylates, the product has, in general, been obtained, in the form of a solid cake, which is difficult to use in subsequent reactions. On the contrary, the process of the present invention yields a product which is finely divided, and which is thus in a form eminently suitable for use in subsequent reactions.

In co-pending U. S. application Serial No. 419,600, there is disclosed and claimed a process for the production of di-alkali metal derivatives of dialkyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylates, which comprises contacting a lower aliphatic diester of succinic acid with an alkali metal alkoxide in the presence of at least one organic diluent, which is a liquid under the reaction conditions, selected from the group consisting of hydrocarbons and dialkyl succinates.

The di-alkali metal derivatives of the present invention are well-known in the art and have many and varied well-known uses. They are in addition suitable for use as intermediates in the production of terephthalic acid and esters thereof by the procedures described in copending applications, Serial Nos. 419,576 and 419,578, filed March 29, 1954.

The present invention provides an improved process in which the product is not only in an eminently suitable form for use in subsequent reactions, but in which the yield of product is higher than in the processes previously disclosed.

According to the present invention, there is provided a process for the production of di-alkali metal derivatives of dialkyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylates, which comprises contacting a lower aliphatic di-ester of succinic acid with an alkali metal alkoxide in the presence of an organic diluent, which is a liquid under the reaction conditions, the said diluent being an ether having a boiling point of at least 90° C.

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It is a feature of the present invention that the alkoxide may be employed alone, or dissolved in a lower aliphatic alcohol, which is conveniently the alcohol corresponding to the alkoxide. If an alcohol is employed together with the alkoxide, this alcohol should be removed after the succinate and alkoxide have been contacted.

Di-esters which are specially suitable for use in the process of the present invention are dimethyl and diethyl succinates. Similarly, alkali-metal alkoxides which are specially suitable are methoxides and ethoxides, sodium methoxide and sodium ethoxide being particularly suitable. If a lower aliphatic alcohol is used as a solvent for the alkoxide, it is convenient for this alcohol to correspond to the alkoxide employed. Thus, if sodium methoxide is used, it is desirable for methanol to be employed as solvent; similarly, if sodium ethoxide is used, ethanol is a suitable solvent.

Ethers suitable for use in the present invention are, for example, di-n-propyl ether, di-n-butyl ether, di-isobutyl ether, di-sec. butyl ether and higher ethers. It is also possible to use ethers containing two oxygen atoms, such as ethylene-glycol dimethyl ether. However, the preferred ether for use in the process of the present invention is 1,4-dioxan (diethylene dioxide).

In the process of the present invention, it is desirable to use a volume of ether which is greater than the volume of succinate employed. In particular, it is desirable to use an ether:succinate volume ratio of the order of 2.5:1 to 10:1, and preferably of 3:1 to 5:1. Furthermore, it is desirable to use a succinate:alkoxide molar ratio of the order of 1:1.

The reaction is carried out by heating together the dialkyl succinate, the alkoxide and the ether diluent. When using sodium methoxide in the presence of methanol as the condensing agent, and dimethyl succinate as the ester, the reaction is initially carried out at about 65° C., i. e., the boiling point of methanol. At this temperature, the excess of methanol distills off; the temperature gradually rises until it approaches the boiling point of the ether; it can then be assumed that the reaction is complete.

When using dioxan as a diluent, the product from the reaction is a dispersion of the di-sodium derivative of the dimethyl ester of cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylic acid in a single liquid phase, providing that the preferred ratio of reactants and diluents is employed, the said liquid phase comprising dioxan and unchanged dimethyl succinate. The di-sodium derivative may be separated by filtration; the filtrate comprises dioxan and unchanged ester; these may be recycled to the condensation stage, or they may be separated by distillation.

The removal of methanol from the reaction mixture is readily effected, since the boiling points of methanol and dioxan are 64.6° C. and 101.5° C. However, when ethanol is present in the reaction mixture, the removal of this requires better fractionation, since ethanol boils at a higher temperature than methanol, viz., 78.5° C.

When using a hydrocarbon diluent for effecting the dialkyl succinate condensation, as described and claimed in co-pending U. S. application Serial No. 419,600 yields based on the amount of dialkyl succinate consumed of at most 60% are obtained. Similarly, when using an excess of dialkyl succinate as diluent, yields based on the amount of dialkyl succinate consumed are not appreciably higher. On the contrary, the yield of the dialkali metal derivative of dialkyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylate obtained in the process of the present invention exceeds 80%, based on the amount of dialkyl succinate consumed.

On acidifying the di-alkali metal derivative of dialkyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylate to give the free diol, for example, dimethyl cyclohexa-1,4-diene-2,5-diol-1,5,1,4-dicarboxylate, it is of note that this diol is

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obtained in a colourless form. In previous processes, it has in general been yellow in colour, in spite of operating in a nitrogen atmosphere. It is believed that the yellow colour is attributable to autoxidation, and the presence of the ether diluent inhibits this autoxidation.

Example 1

46 grams of sodium metal were dissolved in 500 ml. dry methanol contained in a 3 litre flask. 292 gm. (260 ml.) of dimethyl succinate and 900 ml. of dry dioxan were now added. The mixture was heated on a bath maintained at a temperature of 80° to 100° C., and a stream of dry nitrogen was passed through the flask. The methanol was completely removed via the distillation column attached to the flask. In effecting the complete removal of methanol, some 30 ml. of dioxan were also distilled over. The reaction mixture was now refluxed under nitrogen for one hour. From the final mixture, the disodium derivative of cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylate was filtered off. On adding this di-sodium compound to 2 litres of 10% by weight hydrochloric acid, 179.2 grams of dimethyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylate were obtained, melting point 154° to 156° C. This corresponds to a yield of 79% based on the amount of sodium used.

The filtrate was distilled to recover dioxan; 25.0 gm. of high-boiling residue remained behind, of which 20.0 gm. were dimethyl succinate. Thus, the yield of dimethyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylate, based on the amount of dimethyl succinate converted, was 84.5%.

Example 2

46 grams of sodium metal were dissolved in 600 ml. of ethanol, and a mixture of 348 gm. of di-ethyl succinate and 1000 ml. of dioxan were added. The mixture was heated as described above; dioxan removed at the same time as the ethanol was replaced from time to time. The reaction product was worked up as described above. 219 grams of di-ethyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylate, m. pt. 127° to 129° C., were isolated, this corresponding to a yield of 86% based on the amount of sodium ethoxide employed. From the dioxan filtrate, 5.4 gm. of di-ethyl succinate were removed. Thus, the yield of di-ethyl cyclohexa-1,4-diene-2,5-diol-1,4-dicar-

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boxylate, based on the amount of di-ethyl succinate converted, was 87%.

I claim:

1. A process for the production of di-alkali metal derivatives of dialkyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylates, which comprises the step of contacting a lower aliphatic di-ester of succinic acid with a solution of an alkali metal alkoxide in an alcohol, in the presence of an amount of dioxane such that the dioxane:di-ester volume ratio is within the limits 2.5:1 to 10:1 and at a temperature which is initially of the order of the boiling point of the alcohol.

2. The process of claim 1 in which the alkoxide employed is sodium methoxide and the alcohol employed is methanol.

3. The process of claim 1 in which the alkoxide employed is sodium ethoxide and the alcohol employed is ethanol.

4. The process of claim 1 in which the dioxane:di-ester volume ratio is within the limits from 3:1 to 5:1.

5. The process of claim 1 in which the di-ester:alkoxide molar ratio is of the order of 1:1.

6. A process for the production of the di-sodium derivative of dimethyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylate which comprises the step of contacting dimethyl succinate with a solution of sodium methoxide in methanol, in the presence of an amount of dioxane such that the dioxane:di-ester volume ratio is within the limits 3:1 to 5:1 and at a temperature which is initially 65° C. and finally of the order of 100° C.

7. A process for the production of the di-sodium derivative of di-ethyl cyclohexa-1,4-diene-2,5-diol-1,4-dicarboxylate which comprises the step of contacting di-ethyl succinate with a solution of sodium ethoxide in ethanol, in the presence of an amount of dioxane such that the dioxane:di-ester volume ratio is within the limits 3:1 to 5:1 and at a temperature which is initially 80° C. and finally of the order of 100° C.

References Cited in the file of this patent

"Organic Reactions," vol. I, Adams, ed., pp. 275, 278, 295 (1942).