April 30, 1974 CHISEKI YOSHIKAWA ET AL 3,808,260

PROCESS FOR PRODUCING ALKYL CHRYSANTEMATES

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Fig. 1

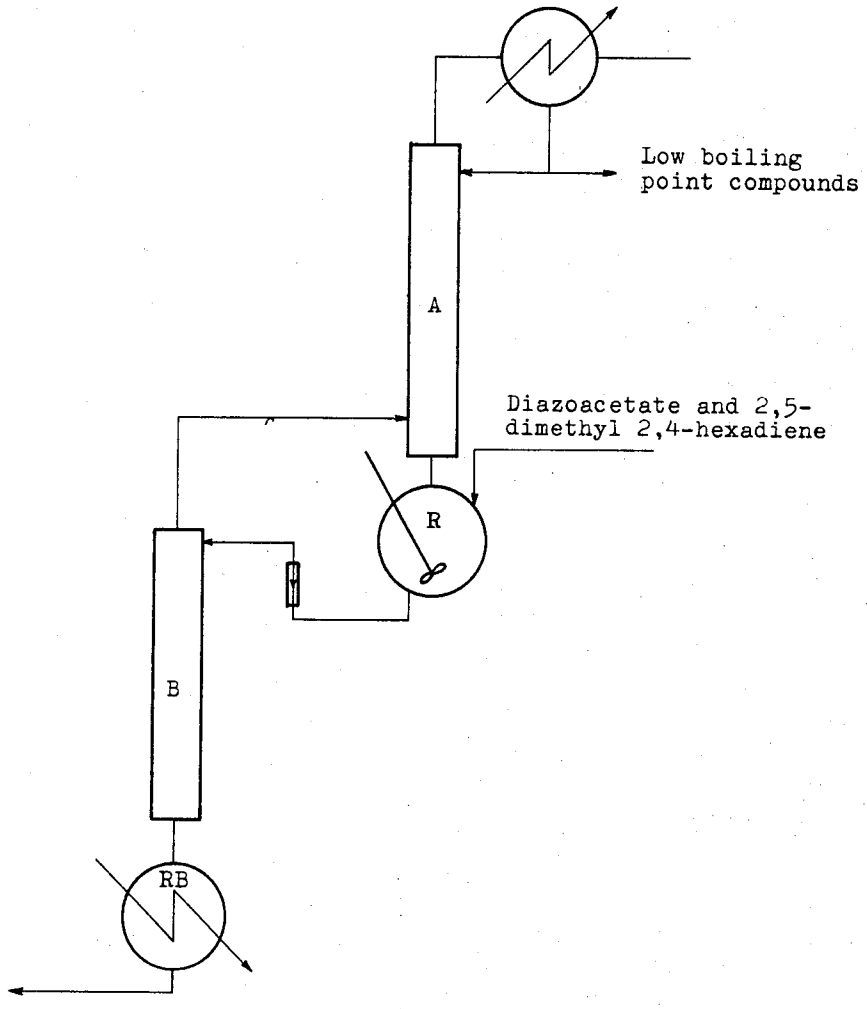

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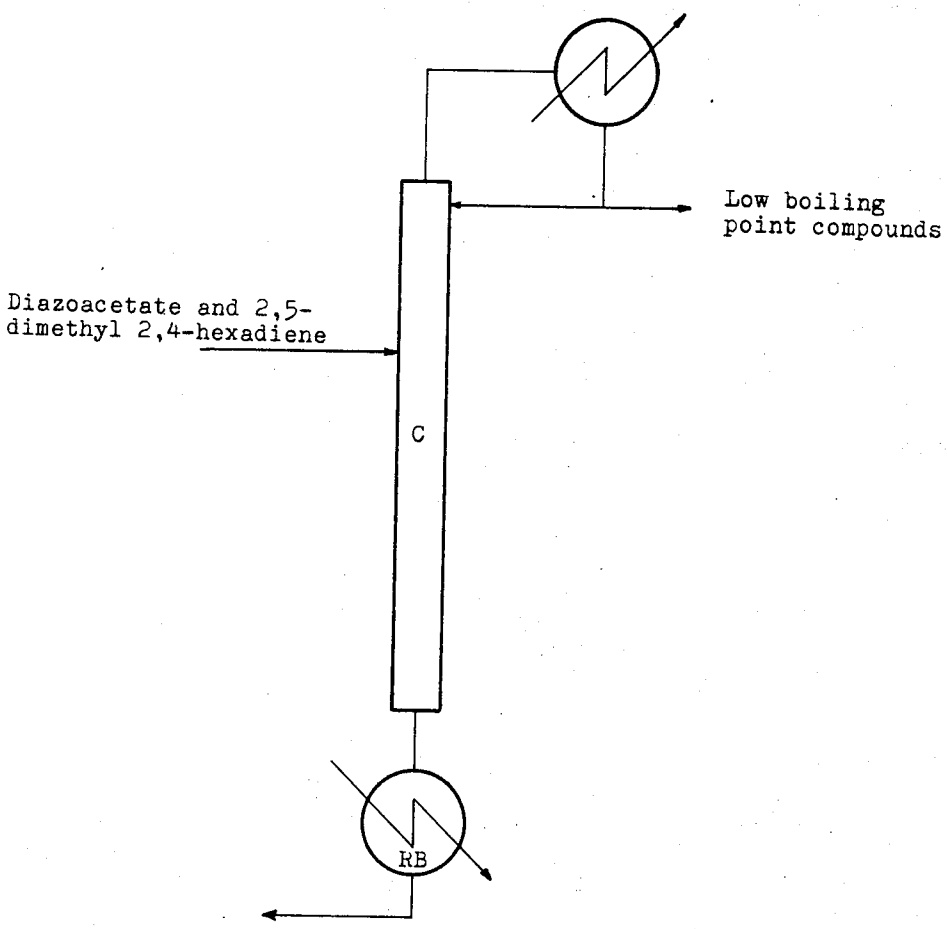
Fig. 2



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PROCESS FOR PRODUCING ALKYL CHRYSANTHEMATES

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Int. Cl. C07c 69/74
U.S. Cl. 260—468 H 9 Claims

ABSTRACT OF THE DISCLOSURE

An alkyl chrysanthemate is obtained in high yield by reacting an alkyl diazoacetate with a great excess amount of 2,5-dimethyl 2,4-hexadiene in the presence of a copper catalyst, while the reaction product is taken out of the reaction zone as much as possible.

The present invention relates to a process of producing alkyl chrysanthemates [alkyl 2,2 - dimethyl - 3(2-methyl-1-propenyl)-cyclopropanecarboxylates] from an alkyl diazoacetate and 2,5-dimethyl 2,4-hexadiene. More particularly, the present invention relates to a process of continuous production of alkyl chrysanthemates in a high yield wherein the reaction of 2,5-dimethyl 2,4-hexadiene with an alkyl diazoacetate is carried out by using a great excess amount of 2,5-dimethyl 2,4-hexadiene, and also to an apparatus for the production thereof.

The term "alkyl" in this invention means a lower alkyl group having up to 4 carbon atoms. The alkyl chrysanthemates are essential intermediate compounds for producing the pyrethroid type insecticides such as allethrin, phthalthrin, etc. As a general method of production thereof, there is known a method wherein a copper powder catalyst is added to 2,5-dimethyl 2,4-hexadiene and then the alkyl diazoacetate is added dropwise, the method being, for example, disclosed by Campbell and Harper in Journal of the Chemical Society, 1945, page 283.

However, it is difficult to obtain the alkyl chrysanthemates in a high yield because several size reactions take place competitively with the formation of maleic ester, fumaric ester, cyclopropane tricarboxylic ester, etc.

The present inventors have studied the basis of reaction and have found that it is necessary to use a great excess amount of 2,5-dimethyl 2,4-hexadiene and take the reaction product out of the reaction zone as much as possible in order to obtain the alkyl chrysanthemates in a high yield by preventing side reactions. On this finding, the present inventors have further studied the process for the production of the alkyl chrysanthemate with industrial advantages and have found that when a solution of the alkyl diazoacetate in 2,5-dimethyl 2,4-hexadiene is fed continuously to the reaction zone comprising 2,5-dimethyl 2,4-hexadiene and a copper catalyst, while the resulting alkyl chrysanthemate is continuously taken out of the reaction zone, the alkyl chrysanthemate can be obtained in a high yield with industrial advantages.

In carrying out the process of the present invention, 2,5-dimethyl 2,4-hexadiene is fed to a reaction zone in which a copper catalyst is placed, and is heated to a temperature not lower than 100° C., preferably 100 to 140° C., more preferably 120 to 140° C. Successively, a solution of an alkyl diazoacetate in 2,5-dimethyl 2,4-hexadiene is fed continuously to the reaction zone, and on the other hand the resulting alkyl chrysanthemate is continuously taken out of the reaction zone together with excess amount of 2,5-dimethyl 2,4-hexadiene and a small amount of a by-product, while a part of 2,5-dimethyl 2,4-hexadiene so taken out is fed back to the reaction zone. The alkyl

chrysanthemate may be separated by means of a conventional procedure, for example, by use of a rectifying column, from 2,5-dimethyl 2,4-hexadiene, which may be reused for dissolving the alkyl diazoacetate.

The amount of the alkyl diazoacetate is 0.01 to 0.1 mole per mole of 2,5-dimethyl 2,4-hexadiene. The concentration of the alkyl diazoacetate in 2,5-dimethyl 2,4-hexadiene is not critical, but preferably is 20 to 70% by weight. As the catalyst, there may be used copper, a powder or granule containing copper, or a copper net.

The invention will be explained more concretely by referring to the accompanying drawings wherein:

FIG. 1 is a diagram of an apparatus useful in carrying out one embodiment of this invention, and

FIG. 2 is a diagram of an apparatus useful in carrying out another embodiment of this invention.

Generally, the process of the present invention may be carried out in the following two manners, i.e. method I wherein the apparatus of FIG. 1 is used and method II wherein the apparatus of FIG. 2 is used.

(I) As shown in FIG. 1, a reactor R is provided between a first column A which separates 2,5-dimethyl 2,4-hexadiene from low boiling compounds and a second column B which separates 2,5-dimethyl 2,4-hexadiene from the alkyl chrysanthemate and by-products. High purity 2,5-dimethyl 2,4-hexadiene which has been separated from low boiling point compounds is supplied as a reflux into the reactor R in which a copper catalyst or a catalyst containing copper has been placed. A solution of the alkyl diazoacetate in 2,5-dimethyl 2,4-hexadiene is added thereto dropwise. The amount of the alkyl diazoacetate is from 0.1 mole to 0.01 mole, preferably from 0.04 to 0.02 mole, per mole of 2,5-dimethyl 2,4-hexadiene supplied to the reactor. The reaction mixture freed from the catalyst by filtration or sedimentation, is led to the second column B from the reactor R. The reaction time, which is indicated by the average retention time, is suitably selected within the range of 5 to 120 minutes and is determined depending on the mole ratio of the alkyl diazoacetate to 2,5-dimethyl 2,4-hexadiene. The preferable range is from 20 to 60 minutes when the mole ratio is 0.04 to 0.02 mole. From the reaction mixture led to the column B, a part of 2,5-dimethyl 2,4-hexadiene is recovered from the top of column B and returned to the bottom of the first column A or to the reactor R for recycling use. The resulting mixture taken out of a reboiler RB may be subjected to a conventional procedure, for example, to rectification, whereby the alkyl chrysanthemate can be obtained continuously in a high yield, and a remaining part of 2,5-dimethyl 2,4-hexadiene may be reused for the above mentioned process.

(II) As shown in FIG. 2, there is used a reaction column which is packed with copper or a filler containing copper, and which is provided with an inlet at a suitable height of the column, and is connected to a reboiler RB at the bottom thereof. The upper part of the column C higher than the inlet has a function of separation of 2,5-dimethyl 2,4-hexadiene from low boiling point compounds, while the part of the column C lower than the inlet constitutes both a reaction zone and a rectifying zone in which a part of 2,5-dimethyl 2,4-hexadiene is separated from the reaction mixture containing the alkyl chrysanthemate. A solution of the alkyl diazoacetate in 2,5-dimethyl 2,4-hexadiene is fed continuously to the reaction column through the inlet, while 2,5-dimethyl 2,4-hexadiene is fed in advance to the reboiler RB, which is heated to cause distillation of 2,5-dimethyl 2,4-hexadiene. The resulting mixture containing the alkyl chrysanthemate and a remaining part of 2,5-dimethyl 2,4-hexadiene is continuously taken out of the reboiler RB, and may be subjected to the conventional procedure, for example, to the rectification, whereby the alkyl chrysanthemate can be

obtained continuously in a high yield, and the remaining part of the 2,5-dimethyl 2,4-hexadiene may be reused for the above mentioned process. The amount of the alkyl diazoacetate is from 0.1 mole to 0.01 mole, preferably from 0.04 to 0.02 mole, per mole of 2,5-dimethyl 2,4-hexadiene refluxed. The reaction time, indicated by the value calculated by dividing the holdup of the reaction column by the reflux amount per minute, is suitably selected within the range of from 5 to 120 minutes and is determined depending on the mole ratio of the alkyl diazoacetate to 2,5-dimethyl 2,4-hexadiene. The preferable range is from 10 to 30 minutes when the ratio is 0.04 to 0.02 mole.

The present invention will be explained in more detail with reference to the following examples, which are only illustrative rather than limitative.

EXAMPLES 1, 2 and 3

The apparatus is arranged as shown in FIG. 1. The reactor R is equipped with a means of sedimentation separation for separating the catalyst, through which the reaction mixture is passed. First, a predetermined amount of 2,5-dimethyl 2,4-hexadiene is charged in the reboiler RB and the reactor R. While the reactor R is then heated for distillation, 30% solution of ethyl diazoacetate in 2,5-dimethyl 2,4-hexadiene is added dropwise to the reactor. The reaction conditions and the results are as shown below.

Example number	1	2	
Reaction temperature, ° C	133	133	133
Amount of 2,5-dimethyl 2,4-hexadiene, moles/hr.	16.9	25	20
Amount of ethyl diazoacetate, mole/hr	0.675	0.675	0.675
Amount of catalyst with respect to the reaction mixture, percent	[a] 5	[a] 5	[b] 5
Reaction time, hr	0.5	0.5	0.2
Yield of ethyl chrysanthemate with respect to ethyl diazoacetate, percent	87.1	93.6	97.3
Yield of ethyl chrysanthemate with respect to 2,5-dimethyl 2,4-hexadiene, percent	94.6	94.7	95.2

[a] Copper powder. [b] Copper net.

EXAMPLE 4

The apparatus is arranged as shown in FIG. 2. The column C is packed with single helix rings. First, a predetermined amount of 2,5-dimethyl 2,4-hexadiene is charged in the reboiler RB which is then heated for distillation. On the other hand, 30% solution of ethyl diazoacetate in 2,5-dimethyl 2,4-hexadiene is supplied from the supply inlet to cause the reaction. The reaction conditions and the result are as shown below.

Reaction temperature ____° C__	133–136
Reflux amount of 2,5-dimethyl 2,4-hexadiene ____moles/hr__	2.1
Amount of ethyl diazoacetate ____mole__	0.06
Reaction time ____hour__	0.32
Yield of ethyl chrysanthemate with respect to ethyl diazoacetate ____percent__	94.1
Yield of ethyl crysanthemate with respect to 2,5-dimethyl 2,4-hexadiene ____percent__	94.9

REFERENCE EXAMPLE

In a flask equipped with a reflux cooling column and a dropping funnel, 2,5-dimethyl 2,4-hexadiene and a copper powder catalyst are charged. Then 50% solution of ethyl diazoacetate in 2,5-dimethyl 2,4-hexadiene is added thereto. The reaction conditions and the result are as shown below.

Reaction temperature ____° C__	127–133
Amount of 2,5-dimethyl 2,4-hexadiene ____g__	100
Ethyl diazoacetate ____g__	100
Reaction time (dropping time) ____hours__	2
Yield of ethyl chrysanthemate with respect to ethyl diazoacetate ____percent__	69.4
Yield of ethyl crysanthemate with respect to 2,5-dimethyl 2,4-hexadiene ____percent__	92.4

What is claimed is:

1. In a process for producing an alkyl chrysanthemate by reacting 2,5-dimethyl 2,4-hexadiene with an alkyl diazoacetate in the presence of a copper catalyst, the improvement which comprises continuously feeding a solution of the alkyl diazoacetate in 2,5-dimethyl 2,4-hexadiene to a reaction zone containing 2,5-dimethyl 2,4-hexadiene and a copper catalyst, continuously removing the resulting reaction mixture containing the alkyl chrysanthemate from the reaction zone, and separating the alkyl chrysanthemate from the reaction mixture, the temperature in the reaction zone being maintained at not lower than 100° C.

2. A process according to claim 1, wherein (1) 2,5-dimethyl 2,4-hexadiene is fed to the reaction zone containing the copper catalyst, which reaction zone is connected to a lower part of a first column and to an upper part of a second column connected to a reboiler, (2) the solution of alkyl diazoacetate in 2,5-dimethyl 2,4-hexadiene is continuously fed to the reaction zone, which is heated to a temperature not lower than 100° C., 2,5-dimethyl 2,4-hexadiene being separated from low boiling compounds in the first column and fed back to the reaction zone as a reflux, the reaction mixture being continuously led to the second column wherein a part of the 2,5-dimethyl 2,4-hexadiene is separated from the resulting mixture and is fed back to the first column, and (3) the resulting mixture is removed from the reboiler and is subjected to rectification to obtain the alkyl chrsyanthemate.

3. A process according to claim 1, wherein the solution of alkyl diazoacetate in 2,5-dimethyl 2,4-hexadiene is continuously fed to a column, packed with a copper catalyst, through an inlet provided in the column, while 2,5-dimethyl 2,4-hexadiene is fed in advance to a reboiler which is connected to the bottom of the column and is heated to cause distillation of the 2,5-dimethyl 2,4-hexadiene, low boiling compounds being removed from the top of the column, and the resulting mixture separated from a part of the 2,5-dimethyl 2,4-hexadiene at the lower part of the column is continuously removed from the reboiler and is subjected to rectification to obtain the alkyl chrysanthemate.

4. A process according to claim 1, wherein the alkyl diazoacetate is fed to the reaction zone in an amount of 0.01 to 0.1 mole per mole of 2,5-dimethyl 2,4-hexadiene.

5. A process according to claim 1, wherein the reaction time for the reaction of 2,5-dimethyl 2,4-hexadiene with the alkyl diazoacetate is 5 minutes to 120 minutes.

6. A process according to claim 1, wherein the temperature in the reaction zone is maintained at 100 to 140° C.

7. A process according to claim 1, wherein the concentration of the alkyl diazoacetate in the solution is 20 to 70% by weight.

8. A process according to claim 2, wherein the reaction time, as indicated by an average retention time, is within a range of 5 to 120 minutes.

9. A process according to claim 3, wherein the reaction time as indicated by a value calculated by dividing the holdup of the column by the reflux amount per minute, is within 5 to 120 minutes.

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