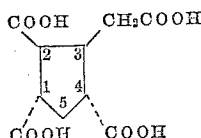


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**PROCESS FOR THE PREPARATION OF TRANS,CIS,
TRANS-1,2,4-TRICARBOXY - CIS - 3 - CARBOXY-
METHYLCYCLOPENTANE**
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The present invention relates to a new alicyclic tetra-carboxylic acid and to its dianhydride. More particularly, the present invention relates to a new geometric isomer of 1,2,4-tricarboxy-3-carboxymethylcyclopentane and to the dianhydride thereof.

The four ring substituents of 1,2,4-tricarboxy-3-carboxymethylcyclopentane may be arranged in a variety of different configurations with respect to each other depending upon which side of the plane of the alicyclic nucleus they are situated. The present invention involves the 1,2,4 - tricarboxy - 3 - carboxymethylcyclopentane in which a pair of the ring substituents lie on one side of the alicyclic nucleus and the remaining pair lie on the opposite side. In this arrangement, it may be said that one pair of the ring substituents are trans with respect to the other pair. According to this terminology, the new acid of the present invention may be designated as trans,cis,trans-1,2,4 - tricarboxy - cis - 3 - carboxymethylcyclopentane. Another, perhaps more appropriate manner of naming this compound is with the use of parenthetical arrows to indicate the relative positions of the various ring substituents. According to this system of nomenclature, the new isomer of the present invention would be 1(↓),2(↑),4(↓)-tricarboxy-3(↑)-carboxymethylcyclopentane. Diagrammatically, this compound may be represented by the following structural formula:



in which the two substituents attached to the ring by solid lines lie on the same side of the plane of the ring which is opposite to the side on which the substituents attached by dotted lines lie.

It is an object of the present invention to prepare a novel isomer of 1,2,4-tricarboxy-3-carboxymethylcyclopentane having the configuration represented by 1(↓),2(↑),4(↓)-tricarboxy-3(↑)-carboxymethylcyclopentane. It is a further object to prepare the dianhydride of 1(↓),2(↑),4(↓)-tricarboxy-3(↑)-carboxymethylcyclopentane. It is a still further object of the invention to prepare these compounds from relatively cheap, readily available starting materials. Other and additional objects will become apparent from a consideration of the ensuing specification and claims.

Broadly speaking, I prepare the new isomer of 1,2,4-tricarboxy-3-carboxymethylcyclopentane by oxidizing 5- or 6-hydroxy-5,6-dihydro-exo-dicyclopentadiene (hereinafter referred to generally as dicyclopentenyl alcohol) or the carboxylic acid esters thereof. Dicyclopentenyl alcohol may be obtained by direct hydration of dicyclopentadiene which, in turn, is readily available in commercial quantities from the high temperature cracking of natural gas and petroleum oils as well as from coal tar. The oxidation may be performed with nitric acid or other suitable oxidizing media in the presence of suitable catalysts.

The invention is illustrated by the following examples:

Example 1

A mixture of 3000 grams of 70% nitric acid and 3.0

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grams of vanadium pentoxide was heated to 60° C. and 1.0 gram of sodium nitrite was thereafter added to the mixture. The resultant solution was agitated while 350 grams of dicyclopentenyl alcohol was added dropwise at atmospheric pressure over a period of 12 hours while the temperature was maintained at 60° C. The exothermic nature of the reaction was sufficient to maintain this operating temperature; occasional cooling being required to prevent the temperature from rising. After addition of the alcohol was complete, the solution was allowed to simmer at 60° C. for two hours and was then concentrated by removing 640 grams of distillate under reduced pressure. Upon completion of the concentrating, the pot temperature was a little below 50° C. The solution was cooled and seeded with 1(↓),2(↑),4(↓)-tricarboxy-3(↑)-carboxymethylcyclopentane and permitted to stand undisturbed overnight. The following day, 92 grams of solid product were removed by filtration. Additional product was recovered later on by further concentration utilizing the same procedure.

The product, a white solid, was washed with glacial acetic acid and dried. It was then recrystallized from additional glacial acetic acid. The compound had a melting point of 186-187° C. It was identified by neutral equivalent and infrared absorption techniques as 1(↓),2(↑),4(↓) - tricarboxy - 3(↑) - carboxymethylcyclopentane.

Example 2

Three thousand parts of 70% nitric acid was heated to 55° C. and a few grains (a "pinch") of sodium nitrite was added. Then 350 parts of dicyclopentenyl alcohol was added dropwise, with stirring, over 3 hours at a rate such that the temperature of the mixture did not rise above 60° C. After being stirred for two additional hours at 55-60° C., the reaction mixture was concentrated, at reduced pressure, to a total weight of approximately 1500 parts. After the mixture stood for 2-3 days, the solids which separated were collected on a sintered glass funnel and "sucked" as dry as possible. The filter cake was slurried with 157 parts of acetic acid, filtered, and washed with two 50-part portions of acetic acid. After drying, the white product which weighed 181 parts (29.9% conversion) melted at 182-4° C. Recrystallization from 142 parts of boiling acetic acid gave 148 parts (82% recovery) of 1(↓),2(↑),4(↓)-tricarboxy-3(↑)-carboxymethylcyclopentane which melted at 186-187° C.

Example 3

A pinch of sodium nitrite was added to 3,000 grams of 70% HNO₃ heated to 50° C., and 450 grams of 5- or 6-acetoxy-dihydro-exo-dicyclopentadiene was added dropwise over 3 hours, the temperature being maintained at 55-60° C. The reaction mixture was concentrated under reduced pressure, and the product crystallized upon standing. After slurrying in acetic acid, 191.5 grams of material melting at 181-4° C. was obtained. Upon recrystallization from boiling acetic acid, the melting point was raised to 187-8° C., and the product was identified as 1(↓),2(↑),4(↓) - tricarboxy - 3(↑) - carboxymethylcyclopentane.

Dicyclopentenyl alcohol may be prepared from dicyclopentadiene with 20-25% sulfuric acid according to the technique of Bruson and Riener described in J. Am. Chem. Soc. vol. 67, pages 723-8 (1945). The alcohol is used for the oxidation step rather than the dicyclopentadiene itself because the latter tends to polymerize and char in an oxidizing environment.

The carboxylic acid esters of dicyclopentenyl alcohol may be obtained by direct esterification of the alcohol or by the sulfuric acid catalyzed addition of the acid to dicyclopentadiene, as described in J. Am. Chem. Soc., vol.

67, pages 1178-1180 (1945). Thus, the starting material of Example 2 may be prepared from dicyclopentadiene and acetic acid, or by direct esterification of dicyclopentenyl alcohol with acetic acid. The ester group does not enter into the reaction, and the new compound of the present invention may thus be prepared from dicyclopentenyl alcohol and/or from any ester thereof which is hydrolyzable to the alcohol. The nature or structure of the ester group, i.e., of the acid from which the ester is prepared, is in no sense critical to the invention. For economic reasons, the esters of simple, readily-available aliphatic and aromatic acids, like acetic acid and benzoic acid, are preferred starting materials as is the dicyclopentenyl alcohol itself.

For the oxidation, nitric acid having an initial concentration of about 30-75% is operable. With nitric acid below about 30% concentration, the reaction is too slow to be of any practical significance. Nitric acid stronger than about 75% tends to overoxidize the alcohol which leads to the formation of oxalic acid. Though oxidation with nitric acid represents the preferred procedure, other conventional oxidizing agents are operable including, for example, chromic acid and the like.

A catalyst is not essential to the oxidation. It is often very advantageous, however, since the presence of a catalyst will frequently accomplish better yields at lower temperatures, and sometimes with less nitric acid than would otherwise be required. Suitable catalysts include pulverized cobalt, nickel or vanadium, as well as the oxides of vanadium, tantalum, lead, manganese, cobalt, chromium, and molybdenum, etc.

It has also been found that sodium nitrite tends to promote the reaction by initiating the formation of oxides of nitrogen which tend to encourage the oxidation, as is well-known in the art. This is not a critical feature of the invention, however, inasmuch as the oxidation may be carried out in the absence of sodium nitrite as well as without a catalyst.

Once addition of the dicyclopentenyl alcohol is commenced, the temperature of the reaction mass must be kept below about 75° C. This is necessary in order to prevent overoxidation. The reaction may be conveniently performed anywhere in the range of about 30° to 60° C. and this represents the preferred operating range. Atmospheric pressure is suitable though increased pressure may facilitate the reaction in some instances.

Best yields are obtained if the reaction mass is maintained at the operating temperature for at least about an hour after the addition of the dicyclopentenyl alcohol is completed. In a batch system, the initial run may occasionally not result in the precipitation of any product presumably because of the solubility of the product in the reaction mass. In such cases the reaction mixture may be butted back to about 70% nitric acid, based on the water present, and the oxidizing procedure repeated. At this time, solids begin to appear and the product may be isolated by filtration as indicated above. Subsequent repetition of the oxidation procedure by fortifying the nitric acid to about a 70% concentration each time will give additional product until all of the dicyclopentenyl alcohol has been converted. An alternative method for isolating product from a first-run oxidation mixture yielding no precipitate is to strip off dilute nitric by distillation until the product precipitates sufficiently to be filtered, as illustrated in Example 1.

1(↓),2(↑),4(↓) - tricarboxy - 3(↑) - carboxymethylcyclopentane is a white solid melting at 186-187° C. It is soluble in water and in lower aliphatic alcohols as well as in hydrochloric and glacial acetic acids.

The dianhydride of the acid is somewhat difficult to prepare due to the presence of the methylene group between the carboxyl groups in the 1- and 4-positions. I have found, however, that it is possible to prepare the dianhydride by stirring the free acid with a large excess of acetyl chloride, acetic anhydride or other dehydrating

agents for very long periods. The preparation of the dianhydride by this technique is illustrated by the following example:

Example 4

One part of 1(↓),2(↑),4(↓)-tricarboxy-3(↑)-carboxymethylcyclopentane is treated with 20 parts of acetyl chloride by stirring at room temperature for 3 to 5 weeks. The resulting solution is concentrated under vacuum to complete dryness. The residue is slurried in a small amount of acetyl chloride. The undissolved product is filtered off and washed with benzene. The dianhydride of 1(↓),2(↑),4(↓)-tricarboxy-3(↑)-carboxymethylcyclopentane was obtained in a 39.5% yield, based on the 1(↓),2(↑),4(↓)-tricarboxy-3(↑)-carboxymethylcyclopentane. It melted at 170-172° C. The dianhydride can be converted back to the original acid by hydrolysis.

The tetrabutyl ester of 1(↓),2(↑),4(↓)-tricarboxy-3(↑)-carboxymethylcyclopentane, which may be formed by esterification of 1(↓),2(↑),4(↓)-tricarboxy-3(↑)-carboxymethylcyclopentane with n-butanol, may be used as a plasticizer for nitrocellulose. The dianhydride which is also made from the free acid, for example, by the technique described above, is useful as curing agents for epoxy resins. The cure may be effected by mixing the dianhydride with the resin at moderate temperatures and thereafter curing the mixture in a mold at elevated temperatures, usually in the neighborhood of about 200° C., for a number of hours. The following example illustrates a typical epoxy cure which is effected with the dianhydride of 1(↓),2(↑),4(↓)-tricarboxy-3(↑)-carboxymethylcyclopentane.

Example 5

Twenty grams of a typical commercial epoxy resin sold by the Ciba Co. as "Araldite" 6020 and formed by the condensation of epichlorohydrin with 4,4'-isopropylidenediphenol is mixed with 5.68 grams of the dianhydride of 1(↓),2(↑),4(↓)-tricarboxy-3(↑)-carboxymethylcyclopentane at 80° C. for 10 minutes to give an anhydride/epoxide ratio of 0.55/1. The dispersion was then cured in a mold at 200° C. for 24 hours to give a hard, light brown resin having a heat distortion temperature of 153° C. at 264 p.s.i. fiber stress. The resin showed a flexural strength of 7328 p.s.i. at room temperature, and a flexural modulus of 0.44×10^6 p.s.i. at room temperature. The cured resin is useful as a molding or potting composition, etc.

I have described and illustrated my invention in the foregoing specification. Since many variations may be made in practicing the invention without departing from the spirit or scope thereof I intend to be limited only by the following claims.

I claim:

1. A process for the preparation of trans,cis,trans-1,2,4-tricarboxy-cis-3-carboxymethylcyclopentane which comprises reacting a compound selected from the group consisting of (A) 5-hydroxy-5,6-dihydro-exo-dicyclopentadiene, (B) 6-hydroxy-5,6-dihydro-exo-dicyclopentadiene, (C) the acetic acid ester of 5-hydroxy-5,6-dihydro-exo-dicyclopentadiene, (D) the acetic acid ester of 6-dihydroxy-5,6-dihydro-exo-dicyclopentadiene, (E) the benzoic acid ester of 5-hydroxy-5,6-dihydro-exo-dicyclopentadiene and (F) the benzoic acid ester of 6-hydroxy-5,6-dihydro-exo-dicyclopentadiene with aqueous nitric acid of a concentration in the range of from about 30% to about 75%, at a temperature below about 75° C.

2. The process of claim 1 wherein said compound is 5-hydroxy-5,6-dihydro-exo-dicyclopentadiene.

3. The process of claim 1 wherein said compound is 6-hydroxy-5,6-dihydro-exo-dicyclopentadiene.

4. The process of claim 1 wherein said compound is the acetic acid ester of 5-hydroxy-5,6-dihydro-exo-dicyclopentadiene.

5. The process of claim 1 wherein said compound is

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the acetic acid ester of 6-hydroxy-5,6-dihydro-exo-dicyclopentadiene.

6. The process of claim 1 wherein said compound is the benzoic acid ester of 5-hydroxy-5,6-dihydro-exo-dicyclopentadiene.

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