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DIMERIC FATTY ACIDS

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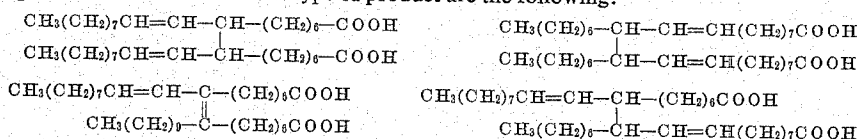
4 Claims. (Cl. 260-407)

The present invention relates to a novel process of producing dimeric fatty acids and esters thereof, and to the resultant products. Polyesters, polyamides, and other derivatives of these dimeric fatty acids possess unusual properties which distinguish them from corresponding products derived from other dimeric fatty acids. The dimeric fatty acids of the present invention are useful in the coating, resin, and fiber fields.

The present invention involves the dimerization of monoolefinic higher fatty acids to produce dimeric, and, to some extent, higher polymeric acids, which retain the unsaturation of the fatty acids from which they are derived. It is thus possible to produce dimeric acids from such unsaturated acids as oleic acid, which do not readily undergo polymerization in the usual thermal polymerization process. In addition, any polymers formed in the usual thermal polymerization of oleic acid are essentially saturated or contain one double bond per dimer molecule, whereas the polymeric acids of the present invention retain the unsaturation of the fatty acids employed.

It is therefore an object of the present invention to provide a novel process of producing dimeric fatty acids and esters thereof from mono-olefinic fatty acids, the polymeric acids retaining the unsaturation of the fatty acid starting material.

It is also an object of the present invention to provide novel dimeric higher fatty compounds derived from



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mono-olefinic acids and containing in the dimer the unsaturation of the original fatty acid.

The process involves the treatment, at temperatures in excess of 50° C., of higher fatty acids or esters thereof having only one double bond in the fatty group, with organic peroxides having the formula ROOR¹, in which R is a tertiary alkyl group and R¹ is selected from the group consisting of tertiary alkyl and tertiary alkyl peroxyalkyl groups. Typical of these peroxides are di-tertiary butyl peroxide; 2,2-bis-t-butylperoxy propane; 2,2-bis-t-butylperoxy butane; 2,2-bis-t-butylperoxy pentane; and 3,3-bis-t-butylperoxy pentane. The process is applicable to the free fatty acids containing from 8 to 22 carbon atoms, to the lower aliphatic esters thereof, as for example, the methyl esters, and to the polyhydric alcohol esters thereof, as for example, the glycerides and the pentaerythritol esters. Any higher fatty acid containing a single point of unsaturation may be employed in the present process. Commercially oleic acid is the principal acid readily available for this purpose, and accordingly the invention will be described with particular reference thereto.

The process involves merely mixing the fatty acid or its ester with the peroxide, and heating the mixture in an inert atmosphere for the required time at the required

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temperature. In order to reduce the time period to a commercially practical point, temperatures in excess of 100° C. are usually employed. Preferably the temperatures are in the neighborhood of 130-150° C., requiring time periods of 12 to 48 hours. At the completion of the reaction period, the reaction product may, if desired, be stripped under vacuum to remove all the decomposition products of the peroxide as well as any monomeric fatty acids or esters present therein. The resultant product is essentially a dimeric acid or dimeric ester and contains smaller quantities of higher polymers. It will be appreciated that the removal of the decomposition products and the monomeric fatty acids or esters is not essential if the product desired is a mixture of monomer and dimer and higher polymers.

Example

The oleic acid employed in this example had an acid number of 198.4, and an iodine number of 88.7. 20 grams (0.071 mol) of this oleic acid and 0.75 g. (0.0051 mol) di-tertiary-butyl peroxide were heated without agitation in sealed bottles under nitrogen. The temperature was maintained at 130° C. for 24 hours. Then an additional 0.75 g. of di-tert-butyl peroxide was added, and the heating was continued for another 24 hours. The reaction mixture was then stripped under vacuum to remove volatile decomposition products. The residue was distilled under high vacuum to remove monomeric acid and to yield a dimeric fraction and a polymeric residue. The following properties were found for the dimeric fraction (theoretical values for a dimer containing two non-conjugated double bonds per molecule of dimer acid are given in parentheses): molecular weight 548 (565); acid number 186.5 (198); iodine number (Rapid Wijs) 91.7 (89.9); sp_α at 231m μ 5.6 (0). This ultraviolet absorption may be due to the presence of a small amount of a conjugated isomer such as (I) below.

Thus it appears that the dimeric material is largely a dimer acid of oleic acid having retained the unsaturation of the original oleic acid. Possible structures for this type of product are the following:

The reaction with the monohydric and polyhydric alcohol esters of mono-olefinic acids proceeds in the same manner and under the same conditions described with reference to the free acid in the example. Similarly, any of the peroxides listed above can be substituted for the di-tertiary-butyl peroxide in the example and the process conducted under the same conditions to produce similar results.

The quantity of peroxide may vary quite widely. The amount of polymer formed appears to be directly proportional to the amount of peroxide employed. If very small quantities are used small quantities of polymer are formed and it may be necessary to strip off large quantities of monomer to obtain a relatively pure or high concentration polymer. Where large quantities of peroxide are employed, there is some tendency for the formation of trimers and higher polymers. In general, from about 5 mol percent to 30 mol percent is preferred. Quantities outside this range may be used with the general effect on results described above.

We claim as our invention:

1. Process of dimerizing a compound selected from the group consisting of higher fatty acids containing only one double bond, and lower aliphatic monohydric alcohol

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esters thereof, which comprises heating said compound to a temperature in excess of 100° C. in the presence of organic peroxide having the formula ROOR¹ in which R is a tertiary alkyls group and R¹ is selected from the group consisting of tertiary alkyl and tertiary alkyl peroxyalkyl groups. 5

2. Process of dimerizing a compound selected from the group consisting of higher fatty acids containing only one double bond, and lower aliphatic monohydric alcohol esters thereof, which comprises heating said compound to a temperature in excess of 100° C. in the presence of di-tertiary-butyl peroxide. 10

3. Process of dimerizing oleic acid which comprises heating oleic acid to a temperature in excess of 100° C. in the presence of di-tertiary-butyl peroxide. 15

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4. Process of dimerizing oleic acid which comprises heating oleic acid to a temperature in the range of 130-150° C. in the presence of di-tertiary-butyl peroxide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,568,426	Whetstone et al. -----	Sept. 18, 1951
2,588,902	Wiebe -----	Mar. 11, 1952

OTHER REFERENCES

Ralston: Fatty Acids & their Derivatives, John Wiley & Sons, N. Y. C., 1948, page 473.