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3,364,248

NOVEL DICYANOETHYLFATTYDIAMINES
OF FATTY ACIDS

Eugene J. Miller, Jr., Wheaton, and Ago Mais, La Grange Park, Ill., assignors to Armour and Company, Chicago, Ill., a corporation of Delaware
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4 Claims. (Cl. 260—465.5)

This invention relates to novel derivatives of fatty acid and more particularly to a novel class of dicyanoethylfattydiamines.

It has long been the desire of chemists to synthesize or to extract from natural substances compounds which not only possess the desirable physical and chemical properties of the long chain fatty acids, but also contain two or more reactive groups therein. With two or more reactive groups, the fatty compound would not only have good hydrophobic characteristics, but also have high potency, depending upon its reactive group type for surfactant, for polymeric or for other chemical activity.

Among the approaches made toward accomplishing such an objective, that disclosed in U.S. 2,813,113 is typical. There the oxidation of oleic acid



to azelaic acid $[\text{HOOC}(\text{CH}_2)_7\text{COOH}]$ is discussed. Unfortunately, chain cleavage occurs in such oxidation. This is undesirable because it cuts down the hydrophobic nature of the resultant compound.

Rowe and Swern of the U.S. Department of Agriculture, in the Journal of the American Oil Chemists Society periodical, volume 37, pages 661 to 668 (1960) report that unsaturated fatty acids may be carboxylated with carbon monoxide. Such a reaction would conserve the hydrophobic nature of the fatty acid, but apparently no further work was done toward discovering new difunctional fatty compounds. This is unfortunate because, as discussed below, it has been found that such difunctional compounds may be synthesized rather easily and they possess many attributes highly desirable for various chemical technologies.

Accordingly, an object of this invention is to provide novel difunctional fatty compounds which are useful in various chemical technologies.

Another object is to provide a novel class of fatty diamines, more particularly, dicyanoethylfattydiamines.

Still another object is to provide novel methods for the manufacture of such dicyanoethylfattydiamines.

A further object is to provide a novel class of compounds which are excellent intermediates for other tetrafunctional fatty compounds having valuable properties for various chemical technologies.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the compound possessing the features, properties, and the relation of elements, which are exemplified in the following detailed disclosure, and the scope of the invention will be indicated in the claims.

It has now been found that a novel class of fatty diamines may be prepared by reacting an aminoalkylfattyamine (described more fully in British 920,514 filed June 30, 1959, and British 985,106 filed Jan. 4, 1962) with acrylonitrile. For example, by reacting aminoethylstearylamine with acrylonitrile in the presence of water, N,N-di-(β -cyanoethyl) aminoethylstearylamine is obtained. Such a compound is useful as an intermediate for forming a di-(aminoalkyl) fatty diamine which is useful as a surfactant, particularly as a flotation agent or an asphalt emulsifier, or as an epoxy curing agent. It also is useful as a bactericide.

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Reference is now made to the following examples which illustrate synthesis of specific dicyanoethylfattydiamines:

Example I.—N,N'-di-(β -cyanoethyl) aminostearylamine

A two-liter four-neck Morton flask equipped with a mechanical stirrer, thermometer and reflux condenser is charged with 142 gms. (0.5 mole) aminostearylamine and 13 gms. water. The temperature is raised to 70° C. and acrylonitrile (59 gms., 1.11 moles) is added with vigorous stirring over a period of one hour. The temperature is maintained at 70° C. during the addition, then raised to 80° C. for an additional two hours. Excess acrylonitrile and water are removed in vacuo to yield 192.4 gms. (98.7% theory) of di-(β -cyanoethyl) aminostearylamine as a light oil.

Analysis.—Neut. equivalent, 198.6 (calc'd. 195); primary amine, 3.3%; secondary amine, 93.6%; tertiary amine, nil.

Example II.—N,N'-di-(β -cyanoethyl) aminomethylstearylamine

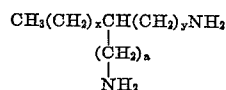
A 250 ml. 3-neck flask equipped with a mechanical stirrer, thermometer, dropping funnel and heating mantle is charged with aminomethylstearylamine (50.0 gms., 0.168 mole; NE, 158.5) and water (4.52 ml., 9% by wt. of amine). The temperature of the reactants is raised to 70° C. and acrylonitrile (19.6 gms., 0.37 mole, 10% excess) added slowly with stirring. The addition is complete in about one hour at 70–80° C. The temperature is then maintained at 76–85° C. for an additional two hours. Water and excess acrylonitrile are removed in vacuo to yield 66.5 gms. (97.5% yield) of N,N'-di-(β -cyanoethyl) aminomethylstearylamine as a pale yellow oil.

Analysis.—Neut. equiv., 212 (calc'd 202.3); secondary amine 92.2%.

The above dicyanoethylfattyamines may be used to prepare polyamines which possess high surfactant activity.

Among the amino- or aminoalkylfattyamines that may be reacted with acrylonitrile in accordance with the method of this invention, those falling within the following formula are operable:

FORMULA I

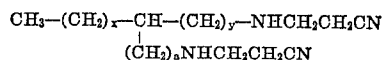


where $a=0$ to 2, x and y are whole numbers and $x+y=6$ to 22.

Such compounds would include the amino-, aminomethyl-, and the aminoethyl-derivatives of fatty amines such as caprylamine, caprylamine, laurylamine, myristylamine, palmitylamine, stearylamine, arachidylamine, behenylamine and lignocerylamine or mixtures thereof such as derivatives from natural fats and oils such as tallow, soybean oil and coconut oil. In general, diamine derivatives of the C_8 to C_{24} fatty acids are useful as a reactant.

The dicyanoethylfattydiamines that may be formed by the method of this invention are those which fall within the following formula:

FORMULA II



where $a=0$ to 2, x and y are whole numbers and $x+y=6$ to 22.

Among compounds which fall within the above formula are N,N'-di-(β -cyanoethyl) aminomethylcaprylamine, N,N'-di-(β -cyanoethyl) aminomethylundecylamine, N,N'-di-(β -cyanoethyl) aminomethylpalmitylamine, N,N'-di-(β -cyanoethyl) aminomethylstearylamine, N,N'-di-(β -cyanoethyl) aminostearylamine, and the like.

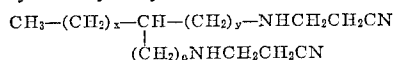
It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above method and in the compounds set forth without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention, which, as a matter of language, might be said to fall therebetween.

Now that the invention has been described, what is claimed as new and desired to be secured by Letters Patent is:

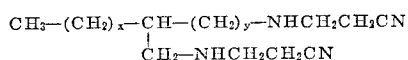
What is claimed is:

1. A dicyanoethylfattydiamine of the formula:



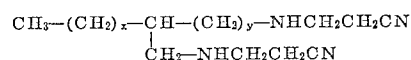
where $a=0$ to 2, x and y are whole numbers and $x+y=6$ to 22.

2. N,N'-di-(β -cyanoethyl) aminomethylpalmitylamine falling within the formula:



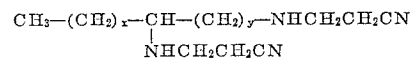
where $x+y=16$, said x and y being whole numbers.

3. N,N'-di-(β -cyanoethyl) aminomethylstearylamine falling within the formula:



where $x+y=16$, said x and y being whole numbers.

4. N,N'-di-(β -cyanoethyl) aminostearylamine falling within the formula:



where $x+y=16$, said x and y being whole numbers.

References Cited

UNITED STATES PATENTS

1,992,615	2/1935	Hoffmann et al. --	260—465.5 X
2,448,013	8/1948	Buc et al. -----	260—465.5
2,965,671	12/1960	Hughes -----	260—465.5
2,982,781	5/1961	Montgomery -----	260—465.5
2,982,782	5/1961	Selcer -----	260—465.5
3,158,643	11/1964	Fulmer et al. ----	260—465.5 X
3,177,254	4/1964	Rogier et al. ----	260—465.5 X
3,264,341	8/1966	Cooperman -----	260—465.5

JOSEPH P. BRUST, *Primary Examiner*.