

UNITED STATES PATENT OFFICE

2,355,442

PROCESS FOR PRODUCING AMINO
ALCOHOL ESTERS

David W. Jayne, Jr., Old Greenwich, and Harold
M. Day, Cos Cob, Conn., assignors to American
Cyanamid Company, New York, N. Y., a corpo-
ration of Maine

No Drawing. Application December 10, 1941,
Serial No. 422,404

4 Claims. (Cl. 260—404)

This invention relates to an improved method for producing alkylol amine derivatives and more particularly relates to an improved method for producing the higher fatty acid esters of alkylol amines which comprises reacting a fatty acid halide with a hydrohalide of a primary or secondary alkylol amine.

The higher fatty acid esters of primary and secondary alkylol amines have in recent years been extensively used in the commercial arts. They have been found to be especially suitable as emulsifying agents, penetrants, detergents, textile treating reagents, and the like.

In spite of the fact that the higher fatty acid esters of primary and secondary alkylol amines are extremely desirable products, no entirely satisfactory method has been developed for producing them, and in many cases where an ester is desired the fatty acid esters of the tertiary alkylol amines such as triethanolamine, have been used instead. In the reaction between a tertiary alkylol amine and a higher fatty acid acylating substance the esters will always be formed because the tertiary nitrogens do not combine with the higher fatty acid acylating substance. In the reaction between an alkylol amine having a primary or secondary amino group the higher fatty acid acylating substance may react with either these amino groups or with the hydroxy groups. Usually the reaction products are made up of a mixture of amides and esters. When a higher fatty acid halide is the acylating agent employed in the reaction with an alkylol amine such as monoethanolamine, the principal product obtained is probably the amide since the primary amino group is more strongly basic than the hydroxy group and reacts preferentially. Various methods have been proposed in the past for reacting higher fatty acid acylating substances with alkylol amines, such as monoethanolamine, to produce esters thereof. One of the methods proposed has been to react a higher fatty acid with an acid salt of monoethanolamine, for example, reacting the acetate of monoethanolamine with oleic acid. In carrying out the reaction considerable difficulty is encountered first due to the incompatibility of the reactants and secondly because relatively high temperatures are employed, temperatures in the neighborhood of 150° C.

In accordance with the present invention we have discovered a process whereby the higher fatty acid esters of primary and secondary alkylol amines are readily obtained and which process avoids the difficulties encountered by the

prior art processes. In carrying out our invention a higher fatty acid halide is reacted with a hydrohalide of a primary or secondary alkylol amine. The reactants are readily compatible and the reaction proceeds smoothly at a temperature of about 70° C. The yields obtained by the process are practically quantitative.

The invention will be more fully described in conjunction with the following specific examples. It should be understood, however, that the examples are given by way of illustration only and the invention is not limited by the details set forth therein. The parts are by weight.

Example 1

A mixture of 231 parts of coconut oil fatty acids chloride, 97.5 parts of anhydrous monoethanolamine hydrochloride and 2 parts of p-toluene sulfonic acid was heated to 70° C. when vigorous evolution of HCl started and the reaction went to completion without further heating. The product was a cream-colored soft wax, practically completely soluble in water. It could be purified by washing with acetone, in which it is practically insoluble. The product was the hydrochloride of the coconut oil fatty acids ester of monoethanolamine.

Example 2

A mixture of 25 parts of myristoyl chloride and 10 parts of anhydrous monoethanolamine hydrochloride and 0.1 part of para-toluene sulfonic acid was heated to 90° C. with evolution of HCl. The product was a white, waxy material, completely soluble in water to give a solution which wet wool and readily foamed.

Example 3

A mixture of 23 parts of coconut oil fatty acids chloride, 17 parts of hydroxyethyl ethylene diamine dihydrochloride, and 0.1 part of p-toluene sulfonic acid was heated to 95° C. with evolution of HCl. The product was a waxy, water-soluble material.

Example 4

A mixture of 23 parts of coconut oil fatty acids chloride, 10 parts of 2-methyl-2-amino propanol hydrochloride and 0.1 part of p-toluene sulfonic acid was warmed to about 80° C. with evolution of HCl. The product was a soft-water-soluble wax.

Example 5

A mixture of 14 parts of coconut oil fatty acids chloride, 10 parts of 2-methyl-2-amino 3-hex-

anol hydrochloride and 0.05 parts of p-toluene sulfonic acid was warmed to 90° C. with evolution of HCl. The product was a water-soluble paste.

Example 6

A mixture of 44 parts of lauroyl chloride, 142 parts of diethanolamine hydrochloride and 0.5 parts of benzene sulfonic acid was heated to 100° C. with evolution of HCl. The product was the half-ester of the diethanolamine hydrochloride. The use of only 71 parts of diethanolamine hydrochloride in the above example will produce the di-ester.

In carrying out the reaction, the temperature may be varied somewhat from that expressed in the actual examples. Preferably it should be below 100° C. Similarly, in the examples a reaction catalyst has been employed and where good yields and low temperatures are desired we prefer to use such a reaction catalyst.

Any higher fatty acid halide or any mixture of fatty acid halides may be employed for carrying out the reaction. The chlorides are preferred over the bromides only because of their cheapness and ready availability. The halides of representative higher fatty acids that may be employed in our process include those such as caprylic acid, caproic acid, capric acid, sebacic acid, behenic acid, arachidic acid, cerotic acid, erucic acid, melissic acid, stearic acid, oleic acid, ricinoleic acid, linoleic acid, linolenic acid, lauric acid, myristic acid, palmitic acid, mixtures of any two or more of the above-mentioned acids or other acids, mixed higher fatty acids derived from animal or vegetable sources, for example, lard, coconut oil, rapeseed oil, sesame oil, palm kernel oil, palm oil, olive oil, corn oil, cottonseed oil, sardine oil, tallow, soya bean oil, peanut oil, castor oil, seal oils, whale oil, shark oil, partially or completely hydrogenated animal and vegetable oils such as those mentioned; hydroxy and alpha-hydroxy higher aliphatic and fatty acids such as i-hydroxy stearic acid, dihydroxy-stearic acid, alpha-hydroxy stearic acid, alpha-hydroxy palmitic acid, alpha-hydroxy lauric acid, alpha-hydroxy coconut oil mixed fatty acids, and the like; fatty acids derived from various waxes such as beeswax, spermaceti, etc.

The primary and secondary alkylol amines generally are suitable for carrying out our process. These alkylol amines may contain only a single primary or secondary amino group and a single hydroxy group, or they may contain a plurality of primary amino groups, secondary amino groups, both primary and secondary amino groups, as well as a plurality of hydroxy groups. When the alkylol amine employed contains only one primary or one secondary amino group and only one hydroxy group, one mol of the alkylol

amine hydrohalide is reacted with one mol of a higher fatty acid halide. If the alkylol amine contains, for example, one secondary amino group and two hydroxy groups, one mol of the hydrohalide of such an alkylol amine may be reacted with two mols of a higher fatty acid halide to produce the di-ester or with one mol of a higher fatty acid halide to produce the half-ester. When the alkylol amine contains a plurality of secondary or primary amino groups all such groups must be blocked by a hydrohalide group before they are reacted with the higher fatty acid halide. It is readily seen therefore that our process may be utilized for producing the esters of any primary or secondary alkylol amine hydrohalides. Among the various alkylol amines that may be used in carrying out our reaction are the mono and diethanolamines such as monoethanolamine, diethanolamine, propanol amines, butanol amines, pentanol amines, hexanol amines, glycerol amines, 1-amino-2, 3-propane diol, 1,2-diamino propanol, hydroxy ethyl ethylene diamine, 1,2-di-(2'-ethanolamino)-ethane, 1,2-di-(2',3'-propan-diol-amino)-ethane, 1,3-di-(2'-ethanolamino)-2-propanol, 1-(mono-amylamino)-2-(N-amyl-N-2'-ethanolamine)-ethane, N-1',2'-diamino-propylamino-2-ethanol, 1,2-di-(ethanolamino)-3-aminopropane, 1,2,3-tri-(ethanolamino)-propane, tri-(mono-methyl-amino-methyl)-ethanol, 1,2-di-(4'-cyclohexanolamino)-ethane and the like.

We claim:

1. A method of producing esters of higher fatty acids and alkylol amine hydrohalides of the group consisting of alkylol amine hydrohalides containing a primary amino group and alkylol amine hydrohalides containing a secondary amino group which method comprises reacting a higher fatty acid halide with an alkylol amine hydrohalide selected from the group consisting of alkylol amine hydrohalides containing a primary amino group and alkylol amine hydrohalides containing a secondary amino group at temperatures of from about 70-100° C. in the presence of a catalyst comprising an aromatic sulfonic acid.

2. A process according to claim 1 in which the alkylol amine hydrohalide is monoethanolamine hydrochloride and the higher fatty acid hydrohalide is coconut-oil fatty acid hydrohalide.

3. A process according to claim 1 in which the alkylol amine hydrohalide is monoethanolamine hydrochloride and the higher fatty acid hydrohalide is a myristoyl hydrohalide.

4. A process according to claim 1 in which the alkylol amine hydrohalide is monoethanolamine hydrochloride and the higher fatty acid hydrohalide is an oleoyl hydrohalide.

DAVID W. JAYNE, JR.
HAROLD M. DAY.