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UNITED STATES PATENT OFFICE

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ESTERS OF ALCOHOL NONTERTIARY AMINES

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17 Claims. (Cl. 260—404)

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This invention relates to the preparation of carboxylic esters of alcohol non-tertiary amines, particularly higher molecular weight fatty acid esters of hydroxy-alkyl primary and secondary amines.

It has heretofore been suggested, as disclosed, for example, in United States Patent No. 2,206,928, in United States Reissue Patent No. 21,530, and in British Patent No. 337,737, to prepare condensation products of higher molecular weight fatty acids with hydroxy-alkyl primary or secondary amines or, in other words, hydroxy-alkyl non-tertiary amines. Instead of employing the free higher molecular weight fatty acids in the condensation reaction, the corresponding halides, anhydrides and esters have been suggested. In all of these cases, the resulting condensation products comprise mixtures of amides and relatively small proportions of esters or mixed-ester amides of the hydroxy-alkyl non-tertiary amines, the amides largely predominating where equi-molal ratios of higher fatty acid and hydroxy-alkyl primary amine are condensed, and the mixed ester-amides largely predominating where an excess of higher fatty acid or the like is employed in the condensation reaction; and no way has been found which is feasible for effecting a separation of the relatively small proportion of esters from the amides and mixed ester-amides. Thus, for example, if monoethanolamine is condensed with an equi-molal amount of lauric acid at elevated temperatures, in excess of 100 degrees C. and particularly at the recommended temperatures of 150 degrees C. to 175 degrees C., or with lauroyl chloride or esters of lauric acid, the resulting condensation products comprise predominantly the lauric acid amide, and relatively small amounts of mixed ester-amide and lauric acid ester of monoethanolamine, which are inextricably mixed with the amide. It has been found that, for certain purposes, the higher molecular weight aliphatic carboxylic acid esters of the hydroxy-alkyl non-tertiary amines, and more particularly the hydrohalide salts of said esters, substantially free of the corresponding amides or mixed ester-amides are necessary but, to my knowledge, no one has heretofore produced such products nor suggested any manner or method for accomplishing such production. The products are not only different in composition but there are also important distinctions in properties and functions in relation to the known condensation products disclosed in the patents referred to hereinabove.

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In accordance with the present invention, substantially quantitative yields of hydrohalide salts of esters of hydroxy-alkyl non-tertiary amines may be produced in a simple and efficacious manner, devoid or substantially devoid of the corresponding amides or mixed ester-amides. The resulting hydrohalide salts of the said esters exhibit properties which readily distinguish them from the condensation products of the prior art which, as stated, consist predominantly of amides or mixed ester-amides.

In general, the novel process comprises reacting a carboxylic acid acyl halide, particularly a higher molecular weight aliphatic or fatty acyl chloride, for example, lauroyl chloride, with an hydroxy-alkyl non-tertiary amine hydrohalide salt, for example, monoethanolamine hydrochloride, in the presence of an acidic catalyst such as sulphoacetic acid or the like, and preferably at relatively low temperatures, that is, below 100 degrees C. The ester is recovered in the form of a hydrohalide salt, in the particular illustration given, as the hydrochloride of the lauric acid ester of monoethanolamine.

In order that those skilled in the art may readily and fully understand the manner in which the invention may be practiced, various specific embodiments thereof are set out hereinbelow. It will be understood that these are merely illustrative and are not to be construed as limitative of the full scope of the invention in any way. Thus, for example, different combinations of reacting ingredients may be employed, changes may be made in the proportions and temperatures of treatment, such as the use of temperatures of about 50 degrees C. or 60 degrees C. coupled with kneading or vigorous stirring, and other changes may be made, such as the use of acyl bromides instead of acyl chlorides, without departing from the principles of the invention as set out hereinabove and in the appended claims:

Example I

To 46.1 grams of coconut oil mixed fatty acid acyl chlorides, 0.5 gram of sulphoacetic acid was added and there was then added 21.0 grams of the hydrochloride of monoethanolamine. The mixture was heated and stirred at 70 degrees C., a violent reaction setting in with evolution of hydrochloric acid. A white, waxy product was obtained consisting primarily of the hydrochloride of the coconut oil mixed fatty acid esters of monoethanolamine. Analysis of said product showed that it contained less than 3% of free

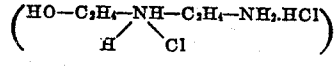
fatty acids and about 101.7% of the theoretical chlorine content, thus showing that the product was quite pure. The product readily dissolves in water to produce a substantially clear solution both in low and in high concentrations.

The coconut oil mixed fatty acid acyl chlorides, used in the example, were prepared in accordance with the method described in my copending application, Serial No. 351,441, filed August 4, 1940, now Patent No. 2,282,320, issued May 12, 1942. In accordance with that method, coconut oil mixed fatty acids or lauric acid or other higher molecular weight aliphatic carboxylic acids are mixed with phosphorous trichloride in a molal ratio of about one mol of the carboxylic acid to preferably about 50% in excess of ⅓ mol of phosphorous trichloride. The resulting mixture is heated slowly, while stirring, to about 60 degrees C. to 90 degrees C., care being exercised to avoid local superheating. The reaction mixture is then allowed to cool to about 40 degrees C. or 50 degrees C. and the lower layer of phosphorous acid is completely drawn off. The upper layer, containing the acyl chloride, is then subjected to a vacuum and a stream of an inert gas such as carbon dioxide is passed through the acyl halide while simultaneously heating at about 130 degrees C. for about one-half hour. This results in removing excess or unreacted phosphorous trichloride and in insuring the preparation of a pure acyl halide. By leaving a small proportion of phosphorous trichloride, for example, about 0.1% to about 0.2%, in the acyl halide product, no extraneous catalyst such as sulphoacetic acid or the like need be employed, the phosphorous trichloride serving to catalytically condition the acyl halide for the reaction.

The sulphoacetic acid used in the example was a crude reaction product obtained by mixing one mol of concentrated sulphuric acid with two mols of acetic anhydride. Pure sulphoacetic acid may be employed with similarly satisfactory results.

Example II

17.7 grams of the hydrochloride of hydroxy-ethyl ethylene diamine



were mixed with 22.0 grams of coconut oil mixed fatty acid acyl chlorides and with 0.6 gram of sulphoacetic acid as a catalyst. The reaction set in at 80 degrees C. and became violent when the temperature was raised to 140 degrees C. The resulting homogeneous product consisted almost entirely of the hydrochloride of the coconut oil mixed fatty acid esters of hydroxy-ethyl ethylene diamine. The product readily dissolves in water to produce a practically clear solution which foams strongly even after acidulation.

The hydrochloride of hydroxy-ethyl ethylene diamine was prepared by adding to 559 grams of concentrated hydrochloric acid 260 grams of hydroxy-ethyl ethylene diamine previously dissolved in 260 cubic centimeters of water. The mass was heated to about 180 degrees C. in vacuo to evaporate the water. The viscous reaction product solidified at room temperature to a hard rock-like substance.

Example III

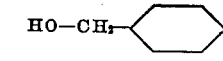
(*a*) To 33.3 grams of diethanolamine hydrochloride there were added 25.3 grams of lauroyl chloride, prepared as described in my aforementioned copending application, and 0.7 gram of sulphoacetic acid as a catalyst. On heating the mixture a reaction set in at a temperature of about 70 degrees C., hydrochloric acid being liberated. The temperature was then raised to 140 degrees C. within a period of a few minutes. On cooling, a solid waxy material was obtained as a layer resting upon a syrupy product of diethanolamine hydrochloride. The waxy material was a crude reaction product consisting mainly of the lauric acid di-ester of diethanolamine hydrochloride. The product was dispersible in hot water and foamed in neutral as well as acidulated water.

(*b*) 7.0 grams of the waxy product of part (*a*) hereof were washed with cold water and then crystallized from 200 cc. of hot isopropyl alcohol. About 4.5 grams of a white crystalline material was obtained. On analysis, its content of ionizable chlorine indicated that the product consisted of substantially pure lauric acid diester of diethanolamine hydrochloride.

Example IV

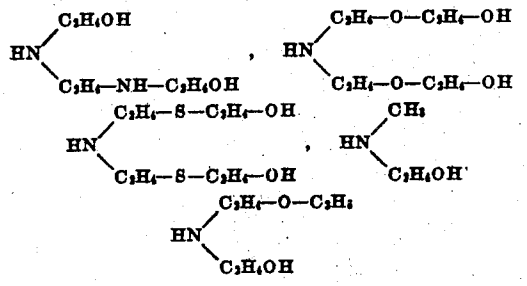
30.4 grams of diethanolamine hydrochloride, 70.0 grams of caprylyl chloride and 0.3 cc. of phosphorous trichloride were mixed together and heated, with stirring. The reaction set in at about 70 degrees C., with the evolution of hydrochloric acid, and was substantially complete at 90 degrees C. within a few minutes. The reaction mixture was then heated up to 120 degrees C. On cooling to room temperature, a solid waxy material was obtained in the form of an upper layer, a small amount of unreacted diethanolamine hydrochloride remaining on the bottom of the reaction vessel. The waxy material, consisting mainly of the caprylic acid diester of diethanolamine hydrochloride, was soluble in cold water. If desired, it may be purified by recrystallization from isopropyl alcohol, as described in Example III.

The alcohol primary and secondary amines, or hydroxy-alkyl primary and secondary amines which, in the form of hydrohalide salts, are utilized in making said salts of the esters may be selected from a large group, including symmetrical, unsymmetrical, normal and iso-derivatives, such as monoethanolamine, diethanolamine, monopropanolamine, dipropanolamine, monobutanolamine, mono-isobutanolamine, monopentanolamine, dibutanolamine, dipentanolamine, mono- and di-hexanolamine, mono- and di-octanolamine, mono- and di-decylolamine, mono-laurylolamine, mono-hexadecylolamine, mono-octadecylolamine, mono-ethyl ethanolamine, mono-butyl ethanolamine; arylolamines and cyclic hydroxy amines such as cyclohexyl ethanolamine, N-cyclohexyl butanolamine, ethanolaniline, phenylethanolamine, p-amino phenol,



2-methylamino-propan-diol-1,3; 1-phenylamino-propan-diol-2,3; 1-hydroxy-ethylamino-2, methoxy-propan-ol-3; 2-N-methylamino-propan-diol-1,3; monoethanol monopropanolamine, monoethanol monobutanolamine, alkylol polyamines such as alkylol derivatives of ethylene diamine, diethylene triamine, and triethylene tetra-amine as, for example, hydroxy-ethyl ethylene diamine; diglycerol mono-amine; diglycerol di-amine; hydroxylamine; hydroxy-amines derived from other polyhydric alcohols, including glycols, sugars and

sugar alcohols such as ethylene glycol, diethylene glycol, dextrose, sucrose, sorbitol, mannitol and dulcitol;



and the like, 1-amino-2,3-propanediol, 2-amino-1,3-propanediol; 2-amino-2-methyl-1,3-propanediol; trimethylol amino methane; 2-amino-2-n-propyl-1,3-propanediol; 2-amino-2-isopropyl-1,3-propanediol; 2-amino-2-methyl-1,4-butanediol; 2-amino-2-methyl-1,5-pentanediol; 2-amino-2-ethyl-1,3-propanediol; 2-amino-2-ethylol-1,3-propanediol; 2-amino-2-methyl-1,6-hexanediol; 1-amino-1,1-dimethyl ethanol; trimethylol amino-methyl methane, trimethylol amino-methylol methane. The glycerol mono-amines and the related hydroxy amines, such as various of those disclosed hereinabove, may be prepared by various procedures and in different ways. Many of them are conveniently produced by nitrating paraffin hydrocarbons, substituting methylol groups for hydrogen on the carbons to which the nitro groups are attached, and then reducing the nitro groups to amine groups. These amine groups may be further alkylated or otherwise substituted if desired. Polymerized hydroxy non-tertiary amines or polymerized hydroxy amines containing hydrogen directly attached to nitrogen and prepared, for example, by polymerizing monoethanolamine or diethanolamine or mixtures thereof, or other hydroxy-alkyl non-tertiary amines such as those mentioned hereinabove, particularly in the presence of a catalyst such as sodium hydroxide or the like, may also be employed. The preparation of polymerized hydroxy amines is disclosed, for example, in United States Patent No. 2,178,173. Homologues and substitution derivatives of the above-mentioned hydroxy amines may also be utilized. It will be understood that the hydroxy-alkyl primary and secondary amines may be utilized in pure, impure or commercial form.

The carboxylic acids whose acyl halides are used in the reaction with the alcohol primary or secondary amines may also be selected from an extensive group including straight chain and branched chain aliphatic (including cyclo-aliphatic) carboxylic acids, saturated and unsaturated, such as butyric acid, 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, dihydroxystearic 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, montan wax, and carnauba wax and carboxylic acids derived, by oxidation and other methods, from petroleum; cycloaliphatic and hydroaromatic acids such as hexahydrobenzoic acid, resinic acids, naphthenic acids and abietic acid; aromatic acids such as phthalic acid, benzoic acid, naphthoic acid, pyridine carboxylic acids; hydroxy aromatic acids such as salicyclic acid, hydroxy benzoic and naphthoic acids, and the like; and substitution and addition derivatives, particularly halogen substitution and addition derivatives of the aforementioned carboxylic substances. It will be understood that acyl halides of mixtures of any two or more of said acids may be employed if desired. The acyl chlorides of the unsubstituted fatty acids having from eight to eighteen carbon atoms are especially satisfactory.

The catalysts may be selected from a large group including, for example, sulphoacetic acid, phosphorous acids, phosphorous trichloride, and the like.

It will be understood that any of the hydrohalide salts of any of the alcohol non-tertiary amines disclosed may be reacted with any of the disclosed carboxylic acid acyl halides in the presence of any of the catalysts.

In general, I prefer to carry out the esterification reaction at a temperature ranging between about 70 degrees C. and 140 degrees C. at atmospheric pressure. It will be understood, however, that the reaction temperature may be varied and that the reaction may be conducted under sub-atmospheric or super-atmospheric pressures if so desired.

The salts of many of the esters possess detergent and surface modifying properties and characteristics. In general, they are not stable in the presence of alkalies. For certain purposes, therefore, it is advantageous to admix or combine them with acid salts such as sodium acid sulphate and the like or with neutral salts such as sodium sulphate. They may, in general, be employed for the uses and purposes for which surface or interface modifying agents have been suggested in the prior art. Thus, for example, they may be utilized for the softening of textiles such as cellulose esters and ethers, rayon, and natural and synthetic fibres. They are especially useful in ore flotation operations, particularly for separating silica from manganese ores and other ores. Many of them possess bactericidal, bacteriostatic, germicidal and like properties which, together with their surface modifying characteristics, may be taken advantage of in dentifrices, cosmetic creams, shaving creams of the lathering and brushless type and the like. They may be utilized in the presence of dilute acids such as hydrochloric acid, sulphuric acid, sulphurous acid, acetic acid, and similar inorganic and organic acids. They may also be employed in the presence of such diverse substances as hydrophilic gums including pectin, tragacanth, karaya, locust bean, gelatin, arabic and the like, glue, vegetable, animal, fish and mineral oils, solvents such as carbon tetrachloride, monoethyl ether of ethylene glycol, monobutyl ether of ethylene glycol, monoethyl and monobutyl ethers of diethylene glycol, cyclohexanol, higher fatty acid partial esters of aliphatic polyhydroxy substances such as mono-caprylin, mono-laurin, lauric acid

mono-esters of ethylene glycol and diethylene glycol, and the like. They may be used together with wetting, emulsifying, frothing, foaming, penetrating and detergent agents such as the higher molecular weight alcohol or alkyl sulphates, phosphates, pyrophosphates and tetraphosphates as, for example, lauryl sodium sulphate, myristyl sodium pyrophosphate, cetyl sodium tetraphosphate, octyl sodium sulphate, oleyl sodium sulphate, and the like; higher molecular weight sulphonic acid derivatives such as cetyl sodium sulphonate and lauryl sodium sulphonate; sulpho-carboxylic acid esters of higher molecular weight alcohols such as lauryl sodium sulphoacetate, dioctyl sodium sulpho-succinate, dilauryl potassium sulpho-glutarate, lauryl monoethanolamine sulpho-acetate, and the like; sulphuric and sulphonic derivatives of condensation products of alkylolamines and higher fatty acids; Turkey red oils; compounds of the type of isopropyl naphthalene sodium sulphonate, and other classes of wetting agents.

The salts of the esters of the present invention may also be employed as intermediates in the preparation of other chemical compounds or derivatives, particularly those having emulsifying, wetting, frothing, sudsing, detergent and, in general, surface or interface modifying properties. Such derivatives include sulphates; sulphonates; phosphates, including pyrophosphates, triphosphates, orthophosphates, tetraphosphates and the like; sulpho-carboxylic acid amides, for example, of such acids as sulphoacetic acid, sulphomaleic acid, sulpho-succinic acid, sulphobenzoic acids, sulpho-phthalic acids; quaternary ammonium and other onium derivatives, and the like.

If desired, the free esters may be recovered from the salts thereof in ways known by those versed in the art, namely, by treating with a base at low temperatures, for example, around 0 degrees C.

The term "higher," as used herein and in the claims to describe carboxylic and fatty acids and the like, will be understood to mean at least eight carbon atoms unless otherwise specifically stated.

While the invention has been described in detail, it is to be understood that the scope thereof is not to be limited other than is set forth in the claims.

This application is a continuation-in-part of my prior application, Serial No. 364,032, filed November 2, 1940.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. A method of preparing hydrochloride salts of higher molecular weight aliphatic carboxylic acid esters of alcohol non-tertiary amines, substantially free of amides of said carboxylic acids with said amines, which comprises reacting a higher molecular weight aliphatic carboxylic acid acyl chloride and a hydrochloride of an alcohol non-tertiary amine in the presence of an acid catalyst.

2. A method of preparing hydrochloride salts of fatty acid esters of aliphatic hydroxy-alkyl secondary amines, substantially free of amides of said fatty acids with said amines, which comprises reacting a fatty acid acyl chloride containing from eight to eighteen carbon atoms and a hydrochloride of an aliphatic hydroxy-alkyl secondary amine in the presence of an acid catalyst at temperatures between about 70 degrees C. and about 130 degrees C.

3. A method of preparing hydrochloride salts of lauric acid esters of diethanolamine, substantially free of lauric acid amides of diethanolamine, which comprises reacting lauroyl chloride and diethanolamine hydrochloride in the presence of an acid catalyst.

4. A method of preparing hydrochloride salts of higher molecular weight fatty acid esters of diethanolamine, substantially free of amides of diethanolamine with said higher molecular weight fatty acids, which comprises reacting an acyl chloride of a higher molecular weight fatty acid and a substantially anhydrous hydrochloride of diethanolamine in the presence of a sulphoacetic acid catalyst and at a temperature between about 70 degrees C. and 140 degrees C.

5. A method of preparing hydrochloride salts of higher molecular weight fatty acid esters of hydroxy-alkyl secondary amines, substantially free of amides of said hydroxy-alkyl secondary amines with said higher molecular weight fatty acids, which comprises reacting substantially equi-molal quantities of an acyl chloride of a higher molecular weight fatty acid and a substantially anhydrous hydrochloride of an hydroxy-alkyl secondary amine in the presence of a small proportion of phosphorous trichloride as a catalyst.

6. A method of preparing hydrohalide salts of carboxylic acid esters of alcohol non-tertiary amines, substantially free of amides of said carboxylic acids with said amines, which comprises reacting a carboxylic acid acyl halide and a hydrohalide salt of an alcohol non-tertiary amine in the presence of an acid catalyst.

7. A method of preparing hydrohalide salts of fatty acid esters of aliphatic hydroxy-alkyl secondary amines, substantially free of amides of said fatty acids with said amines, which comprises reacting a fatty acid acyl halide containing from eight to eighteen carbon atoms and a hydrohalide of an aliphatic hydroxy-alkyl secondary amine in the presence of an acid catalyst at temperatures between about 70 degrees C. and about 130 degrees C.

8. A method of preparing hydrohalide salts of higher molecular weight fatty acid esters of diethanolamine, substantially free of amides of diethanolamine with said higher molecular weight fatty acids, which comprises reacting an acyl halide of a higher molecular weight fatty acid and a hydrohalide salt of diethanolamine in the presence of an acid catalyst.

9. A method of preparing hydrohalide salts of higher molecular weight fatty acid esters of diethanolamine, substantially free of amides of diethanolamine with said higher molecular weight fatty acids, which comprises reacting an acyl halide of a higher molecular weight fatty acid and a substantially anhydrous hydrohalide of diethanolamine in the presence of an acid catalyst and at a temperature between about 70 degrees C. and 140 degrees C.

10. A method of preparing hydrohalide salts of higher molecular weight aliphatic carboxylic acid esters of hydroxy-alkyl primary amines, substantially free of amides of said carboxylic acids with said amines, which comprises reacting a higher molecular weight aliphatic carboxylic acid acyl halide and a hydrohalide salt of an hydroxy-alkyl primary amine in the presence of an acid catalyst.

11. A method of preparing hydrochloride salts of higher molecular weight aliphatic carboxylic acid esters of hydroxy-alkyl primary amines, substantially free of amides of said carboxylic acids with said amines, which comprises reacting a higher molecular weight aliphatic carboxylic acid

acyl chloride and a hydrochloride of an hydroxy-alkyl primary amine in the presence of an acid catalyst.

12. A method of preparing higher molecular weight fatty acid esters of aliphatic hydroxy-alkyl primary amines, substantially free of amides of said fatty acids with said amines, which comprises reacting a fatty acid acyl chloride containing from eight to eighteen carbon atoms and a substantially anhydrous hydrochloride of an aliphatic hydroxy-alkyl primary amine in the presence of an acid catalyst at temperatures between about 70 degrees C. and about 140 degrees C.

13. A method of preparing hydrohalide salts of higher molecular weight fatty acid esters of monoethanolamine, substantially free of amides of monoethanolamine with said higher molecular weight fatty acids, which comprises reacting an acyl halide of a higher molecular weight fatty acid and a hydrohalide salt of monoethanolamine in the presence of an acid catalyst at a temperature below 100 degrees C.

14. A method of preparing lauric acid esters of monoethanolamine, substantially free of lauric acid amides of monoethanolamine, which comprises reacting lauroyl chloride and monoethanolamine hydrochloride in the presence of a sulphoacetic acid catalyst.

15. A method of preparing higher molecular weight fatty acid esters of monoethanolamine, substantially free of amides of monoethanolamine with said higher molecular weight fatty acids, which comprises reacting an acyl chloride of a higher molecular weight fatty acid and a substantially anhydrous hydrochloride of monoethanolamine in the presence of a sulpho-acetic acid catalyst and at a temperature between about 70 degrees C. and 140 degrees C.

16. The hydrochloride of fatty acid esters of hydroxy-ethyl ethylene diamine, substantially free from fatty acid amides of hydroxy-ethyl ethylene diamine, the fatty acid radical of said esters comprising largely the lauric acid radical.

17. A method of preparing higher molecular weight fatty acid esters of hydroxy-alkyl primary amines, substantially free of amides of said hydroxy-alkyl primary amines with said higher molecular weight fatty acids, which comprises reacting substantially equi-molal quantities of an acyl chloride of a higher molecular weight fatty acid and a substantially anhydrous hydrochloride of an hydroxy-alkyl primary amine in the presence of a small proportion of phosphorous trichloride as a catalyst.

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