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AMINO ACRYLATES

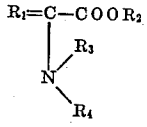
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No Drawing. Application September 23, 1944, Serial No. 555,588

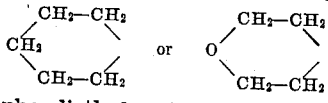
6 Claims. (Cl. 260—482)

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This invention relates to alpha amino esters, and more particularly relates to compounds of the type



where R_1 stands for an alkylidene group, preferably a methylene radical, R_2 is any aliphatic group but generally is an alkyl radical, R_3 and R_4 stand for alkyl, aralkyl or aryl groups, or R_3 and R_4 together stand for an alkylene group, such as



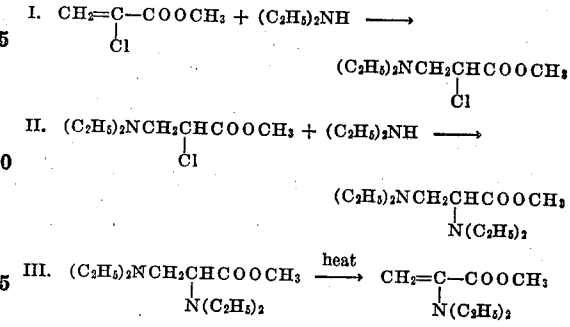
Methyl alpha-diethyl amino acrylate, ethyl alpha dipropyl amino ester of crotonic acid, and butyl alpha diethyl amino ester of beta ethyl acrylic acid, are examples of compounds coming under our invention.

These compounds are useful as textile adjuvants, as well as starting materials for the synthesis of useful organic substances for example, pharmaceuticals.

The compounds of this invention may be made by the heat decomposition of alpha beta diamino esters, particularly of alpha beta diamino fatty acid esters of fatty acids having from two to six carbon atoms inclusive. Suitable compounds of this type include methyl di-ethyl-amino-propionate, ethyl di-dimethyl-amino-butyrate, various compounds shown in the examples and other compounds which will be apparent to those skilled in the art. Suitable temperatures and time of heating vary widely as will be apparent from the examples, but we prefer to effect the decomposition by heating the alpha beta diamino ester at above about 200° C. and not more than about 100° C. above its boiling point at atmospheric pressure. A heating time of between one to five hours gives satisfactory results.

A series of reactions illustrating the preparation of methyl alpha-diethyl amino acrylate as carried out in Example I are given below:

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The following examples further illustrate the invention:

Example I

Methyl α-diethylamino acrylate

378 parts of methyl alpha-chloroacrylate, 250 parts of benzene, 459 parts of diethylamine, and 10 parts of hydroquinone are mixed and refluxed for 8 hours. After filtering the precipitated amine hydrochloride, the filtrate is vacuum distilled. After removal of the benzene, 484 parts of a yellow oil, boiling point 85–105° C. at 4 mm. of pressure. Redistillation of this material yields 227 parts of a liquid consisting of methyl di-diethylamino propionate, boiling point 74° C. at 0.5 mm., n_D^{25} 1.4398,

d_4^{25} 0.911

69 parts of methyl di-diethylamino propionate was decomposed by distilling it through a 12" Vigreux column. The bath temperature was kept at 220–245° C. for 1½ hrs., during which time 11.0 parts of diethyl amine formed and distilled over. The bath temperature was then increased gradually to 280° C. and 53.0 parts of distillate collected, boiling point 130–150° C., over an hour and a half. The 53.0 parts of liquid was distilled in vacuum, and the fraction boiling at 88–96° C. at 20 mm. was collected.

This fraction was redistilled to yield 19.0 parts of methyl α-diethylamino acrylate, 40.2% of the theoretical amount, boiling point 80–91° C. at 20 mm., n_D^{25} 1.4558–1.4563.

EXAMPLE II

Methyl α-diethylamino acrylate

115 parts of methyl di-diethylamino propionate was decomposed by distilling it through a 12" Vigreux column at a bath temperature of 215° C. After 18.1 parts of diethyl amine had been collected, the bath temperature was gradually increased to 280° C. over a 4½ hr. period. 77.1 parts of distillate was collected, boiling point 110–140° C., and a residue of 19.0 parts remained undistilled.

The distillate was refractionated at 20 mm. pressure to yield considerable low boiling material and 9.0 parts of methyl α-diethyl amino acrylate, boiling point 89–96° 11.5% yield. This result indicates that it is important not to run the decomposition reaction over too long a period. Higher yields are obtained when the decomposition reaction is run at a shorter period of time such as for 2 hours at 280° C.

EXAMPLE III

Copolymerization of methyl α-diethylamino acrylate and methyl methacrylate

Mixtures of 75 parts of methyl methacrylate, 25 parts of the amino acrylate, and 2 parts of t-butyl hydroperoxide could be polymerized to a soft, clear, red polymer by heating for a week at 105° C.

Mixtures of 90 parts of methyl methacrylate, 10 parts of amino acrylate, and 2 parts of t-butyl hydroperoxide polymerized to a hard, clear, red resin when heated 1 week at 105° C. Benzoyl peroxide gave a viscous, clear, red liquid under the same conditions.

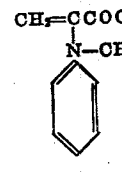
EXAMPLE IV

Methyl alpha-morpholinoacrylate

17.4 parts of morpholine is slowly added to 12.0 parts of methyl alpha-chloroacrylate in 8 parts of benzene containing 0.5 part of hydroquinone. After the initial heat of reaction has subsided, the mixture is refluxed for 22 hours. The 10.6 parts of morpholine hydrochloride formed is filtered off, washed with benzene, and dried to give a white solid, melting point 174° C., 86.6% yield. The filtrate is distilled in vacuo. After removal of the benzene, 12.0 parts of a light yellow distillate was obtained, boiling point 130–150° C. at 0.5 mm. This liquid was then decomposed by heating for two hours at 180° C., producing methyl alpha-morpholinoacrylate.

EXAMPLE V

Methyl alpha-(N-methylanilino)-acrylate



21.4 parts of monomethylaniline, 8 parts of benzene, 12.0 parts of methyl alpha-chloroacrylate, and 0.5 part of hydroquinone were refluxed for 18 hours. Following the removal of benzene by vacuum distillation, there was obtained a fraction of boiling point 80–105° C. at 0.5 mm. This crystallized to a solid of melting point 122-124°, monomethylaniline hydrochloride. Further distillation of the original reaction mixture yielded a light yellow oil. Heat decomposition of this oil for three hours at 180° C. yielded the methyl alpha-(N-methyl anilino) acrylate.

EXAMPLE VI

Methyl alpha-dibenzylaminoacrylate

19.7 parts of dibenzylamine, 6.0 parts of methyl alpha-chloroacrylate, and 0.5 parts of hydroquinone were mixed and allowed to stand for 10 days. Benzene was added, and the white crystalline dibenzylamine hydrochloride, melting point 256° C., was filtered off. 7.8 parts, 66% of the theoretical, was obtained. The benzene was distilled off in vacuo, leaving a transparent, light red, viscous oil. Heat decomposition of this oil at 180° C. for three hours yielded the methyl alpha-dibenzylaminoacrylate.

EXAMPLE VII

Methyl alpha-distearylaminoacrylate

203 parts of distearylamine, 160 parts of benzene, 23.4 parts of methyl alpha-chloroacrylate, and 5 parts of hydroquinone were mixed and heated to refluxing for 7 hours. 106 parts of distearylamine hydrochloride were removed by filtration. That this was the hydrochloride was shown by the precipitation of silver chloride from a warm aqueous silver nitrate solution. The benzene was distilled from the filtrate in vacuo. The residual solid was recrystallized from an alcohol-ether solution and then heated for four hours at 200° C. to give methyl alpha-distearylaminoacrylate.

This application is a continuation in part of our copending application Serial No. 502,023, filed Sept. 11, 1943, now abandoned.

While there have been shown and described certain embodiments of the invention, it is to be understood that it is capable of many modifications. Changes, therefore, may be made without departing from the spirit and scope of the invention as described in the appended claims, in which it is the intention to claim all novelty inherent in the invention as broadly as possible, in view of the prior art.

We claim:

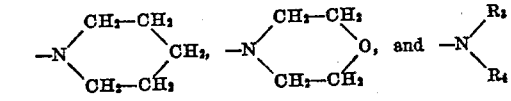
1. A new compound having the formula



wherein R_1 stands for a radical of the group consisting of $CH_2=$, $CH_3-CH=$, and

$$CH_3-CH_2-CH=$$

R_2 is a lower alkyl radical, and X stands for a radical of the group consisting of



wherein R_3 and R_4 stand for radicals of the group consisting of an alkyl, phenyl and benzyl.

2. The method of preparing an alpha dialkyl amino ester of acrylic acid and a lower aliphatic alcohol which comprises heating a lower alkyl ester of an alpha, beta-di- (dialkyl amino) propionic acid to a temperature of between approximately 200° C. and 280° C. for a period of between approximately 1 to 5 hours.

3. The method of preparing methyl alpha diethyl amino acrylate which comprises heating methyl alpha, beta di-(diethyl amino) propion-

ate to a temperature of between approximately 200° C. and 280° C. for a period of between approximately 1 to 5 hours, removing the diethyl amine formed during the heating by distillation and separating from the residue by distillation a fraction having a boiling point of 110 to 150° C. at substantially atmospheric pressure.

4. As a new compound, a lower alkyl alpha morpholino acrylate.

5. As a new compound, a lower alkyl ester of an alpha dialkyl amino acrylic acid.

6. Methyl alpha diethyl amino acrylate.

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