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ALIPHATIC NITRO-COMPOUNDS

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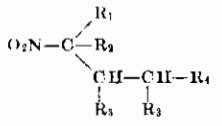
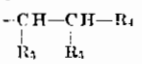
The present invention relates to aliphatic nitro-compounds.

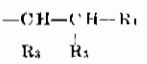
We have found that valuable aliphatic nitro-compounds may be obtained by condensing a nitrile or an ester, for instance the methyl-ester, ethyl-ester or propyl-ester of alpha-beta- unsaturated aliphatic carboxylic acids with primary aliphatic nitro-hydrocarbons. During the reaction of the nitriles, and this being surprising, just as many molecules of nitriles chiefly react with 1 mol of nitro-paraffine as active hydrogen atoms are contained in said nitro-paraffine. As starting material acrylic acid nitrile is particularly used; but moreover the corresponding alkyl derivatives are suitable, for instance crotonic acid nitrile and methacrylic acid nitrile as well as the esters of the corresponding acids. The products thus obtained have the following general formula:



wherein R_1 stands for a substituent of the group consisting of hydrogen, alkyl and



R_2 stands for a substituent of the group consisting of hydrogen and



one R_3 stands for hydrogen, the other R_3 for a substituent of the group consisting of hydrogen and methyl, R_4 stands for a substituent of the group consisting of —CN, —COO—H and —$COOR_5$, R_5 being alkyl.

As nitro-hydrocarbons there may, for instance, be used nitro-methane, nitro-ethane, 1-nitro-propane, 1-nitro-butane or 1-nitro-pentane.

Alkaline substances, such as postassium carbonate, sodium carbonate, caustic soda solution, lime, sodium alcoholate, pyridine and the like have been found suitable as condensing agents. The addition of a solvent or diluent may be advantageous for moderating the reaction and bringing all the components into one phase. It may also be suitable first to introduce the nitrile or the ester and then to cause the nitro-hydrocarbon gradually to run in.

The nitro-polycarboxylic acid nitriles and nitropolycarboxylic acid esters obtained may be used as softening agents or as solvents. If necessary, the nitro-nitriles and nitro-esters are saponified to obtain the corresponding nitro-polycarboxylic acids. The saponification, and this being surprising, readily occurs and the nitro-group is not impaired thereby. Furthermore amino-polynitriles or amino-polycarboxylic acids and the corresponding lactams as well as polyamines are obtained by a reduction or a catalytic hydrogenation. By mild conditions of hydrogenation the corresponding hydroxyl-amino compounds are likewise obtainable. All these substances are of great industrial importance when they are used as such or as intermediate products for softening agents, resins, adjuvants in the textile industry and in the pharmaceutical industry.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto:

(1.) An aqueous solution of 30 grams of potassium carbonate is introduced at a temperature of 15° C–20° C, while stirring, into 1200 grams of acrylic acid nitrile, 1100 grams of alcohol and 450 grams of nitro-methane, whereby reaction sets in with self-heating up to 30° C. Further 450 grams of nitro-methane and an aqueous solution of 30 grams of potassium carbonate are then introduced in the course of about 5 hours at 30° C, while stirring. The mixture is then kept for several hours at 40° C. After 1 to 2 days the large crystals which have separated are filtered with suction, washed and dried. A further portion of crystals is obtained by the addition of water to the filtrate. The yield amounts to 860 grams of nitromethyl-tri-beta-propionic acid nitrile $NO_2.C(CH_2.CH_2.CN)_3$, i. e. 52 per cent of the theoretical yield. White, great prisms are obtained which are sparingly soluble in water and alcohol and melt at 110° C to 112° C.

The corresponding mono-substitution products and di-substitution products (γ-nitro-butyric acid nitrile boiling at 118° C–121° C under a pressure of 3 mm of mercury and nitromethyl-di-beta-propionic acid nitrile $NO_2.CH(CH_2.CH_2.CN)_2$, melting at 60° C–63° C) are likewise obtained in very small proportions, but only when the nitro-methane is used in a very large excess.

Saponification of the nitro-methyl-tri-beta-propionic acid nitrile

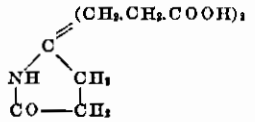
165 grams of nitro-methyl-tri-beta-propionic acid nitrile are boiled for 4 hours in a reflux condenser together with a mixture of 1 kilogram of concentrated hydrochloric acid and 600 cc of

water. When cold the corresponding nitro-methyl-tri-beta-propionic acid

$$NO_2.C(CH_2.CH_2.COOH)_3$$

crystallizes. The yield amounts to 185 grams, i. e. 90 per cent of the theoretical yield. The product melts at 183° C to 186° C.

By a catalytic hydrogenation of said nitro-tri-carboxylic acid the corresponding amino-tri-carboxylic acid or the lactam

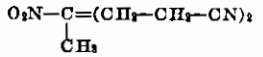


immediately formed therefrom by the separation of water and melting at 159° C–161° C are obtained in a good yield.

Further products may be obtained by a reduction or a catalytic hydrogenation of the nitro-methyl-tri-beta-propionic acid nitrile, for instance aminomethyl-tri-beta-propionic acid nitrile and poly-amines.

(2.) 80 grams of acrylic acid nitrile, 80 grams of alcohol and 38 grams of nitro-ethane are mixed, while stirring. By the addition of a solution of 2 grams of potassium carbonate in 15 cc of water the reaction is started at 12° C–15° C. With self-heating to 40° C–45° C the reaction is chiefly complete after about 1 hour; it is terminated by further heating it for 5 hours to 40° C.

By the addition of water the reaction product is separated in the form of an oil which is washed and dried. Acrylic acid nitrile present in excess is removed by distillation under reduced pressure. The residue from distillation is a thick brownish oil and constitutes the 1-nitro-ethyl-1-di-beta-propionic acid nitrile



It can be distilled only with decomposition. The yield amounts to 60 grams, i. e. 67 per cent of the theoretical yield. If nitro-ethane is used in a large excess there is likewise obtained the γ-nitro-valeric acid nitrile in the form of an oil boiling at 106° C under a pressure of 2 mm of mercury.

By boiling the 1-nitro-ethyl-1-di-beta-propionic acid nitrile with a strong acid the corresponding 1-nitro-ethyl-1-di-beta-propionic acid is obtained.

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