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REACTION OF ETHYLENIMINES WITH THIOLS AND PRODUCT THEREOF

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This invention relates to organic compounds and more particularly to organic sulfides containing an amino group and still more particularly to beta-aminoethyl sulfides.

This invention has as an object the provision of a new and convenient process for the preparation of beta-aminoethyl sulfides. Another object is the provision of a process for the preparation of new compounds having a plurality of beta-aminoethylthio groups. A further object is the new class of compounds having a plurality of beta-aminoethylthio groups. Another object is the provision of a process for making anti-corrosion and anti-sludge agents for lubricating oils. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein an ethylenimine is reacted, under substantially neutral conditions, with a thiol, free from groups, other than thiol, which react with ethylenimines. A preferred modification of the invention is that wherein the thiol contains a plurality of thiol groups. Another phase of the invention is the class of poly-beta-aminoethylthio substituted compounds prepared by the preferred process modification.

In the process of this invention, substantially equimolecular amounts of a thiol and of an ethylenimine are reacted under substantially neutral conditions, at a temperature and for a period of time sufficient to bring about substantially complete reaction. The reaction product is then freed from unchanged reactants, if any are present, and purified by suitable procedures. By substantially neutral conditions is meant that the reaction mixture has an acidity corresponding to that of a mixture containing the free thiol and containing no acidic material other than the thiol. The acidic nature of the thiol is low as is indicated inter alia by the article by Schwarzenbach and Epprecht, Helv. Chem. Acta. 19, 169 (1936).

Although the invention is not to be limited by the following theoretical explanation, it is probable that, under the slightly acidic influence of the mercapto group, the rather unstable ethylenimine ring is opened, with subsequent addition of the thiol to the radical thus formed. The net result of the reaction is represented by the equation:

$$R'SH + CH_2\text{—}CH_2 \longrightarrow R'SCH_2CH_2NHR^2$$
$$\qquad\qquad \diagdown\ \diagup \quad NR^2$$

or, when a polythiol is used:

$$R'(SH)_z + zCH_2\text{—}CH_2 \longrightarrow R'(SCH_2CH_2NHR^2)_z$$
$$\qquad\qquad\qquad\quad \diagdown\ \diagup \quad NR^2$$

The reaction products, which are generically represented by the above formulae, may be designated generally as beta-aminoethyl sulfides. The individual members described in the examples below are perhaps more correctly named (beta-aminoethyl) thioalkanes. These products are solids or liquids and possess a titratable basicity, because of the presence of the amino group or groups.

The more detailed practice of the invention is illustrated by the following examples, wherein parts given are by weight. There are of course many forms of the invention other than these specific embodiments.

Example I

Beta-aminoethylthiopropane

A mixture of 17.2 parts of ethylenimine and 30.4 parts of n-propanethiol is heated in a closed vessel at 100° C. for 20 hours. The reaction product is then subjected to distillation, whereupon a small amount of unchanged starting materials is first removed, then 37 parts of a homogeneous liquid boiling at 84–87° C. at 23 mm. pressure is obtained. This product, a colorless oil, boils on redistillation at 85-86° C. at 25 mm. pressure. Other physical constants are: d^{25}_4: 0.9295; N^{25}_D: 1.4831. Analyses indicate that it is beta-aminoethylthiopropane, $CH_3CH_2CH_2SCH_2CH_2NH_2$.

Calcd. for $C_5H_{13}NS$: S%, 26.89. Found: 26.82, 26.87. Neutralization equivalent (with N/10 HCl in the presence of methyl orange): calcd. 119; found, 119.5.

The yield in beta-aminoethylthiopropane is 78% of the theory. The product is soluble in water and organic solvents such as methanol and benzene.

Example II

1,6-bis-(beta-aminoethylthio) hexane

A mixture of 11 parts of ethylenimine and 18 parts of hexane-1,6-dithiol is heated in a closed vessel, without solvent or added catalyst, at 100° C. for 23 hours. There is obtained, on distillation of the reaction product, 25 parts of an oil boiling around 200° C. at 6 mm. pressure. The product, on redistillation in an atmosphere of nitrogen, boils at 196–200° C. at 2 mm. pressure. It is a pale yellow oil which crystallizes on standing to a solid melting at 38–40° C. Analyses indicate that this product is 1,6-bis-(beta-aminoethylthio)hexane, $NH_2CH_2CH_2S(CH_2)_6SCH_2CH_2NH_2$.

Calcd. for $C_{10}H_{24}N_2S_2$: C, 50.85; H, 10.17; S, 27.12. Found: C, 51.02; H, 10.04; S, 26.74. Neu-

tralization equivalent (with N/10 HCl in the presence of methyl orange): calcd. 236; found 241.

The yield in 1,6-bis-(beta-aminoethylthio)-hexane is 89% of the theory. The product is soluble in water and the common organic solvents.

In the process of the present invention, any thiol free from functional groups, other than thiol, which are capable of reacting with ethylenimines substantially faster than the thiol group, may be used. Examples of such undesired functional groups are the carboxyl, sulfonyl, active halogen, aldehyde, acid chloride group, etc. When such a functional group is present, the reaction product will in general be non-homogeneous and polymeric in character. The invention is applicable to thiols of the formula $R'(SH)_x$, wherein R' is an organic radical of valence x, x being an integer and at least one, said organic radical being free from the undesirable functional groups above indicated. In the preferred subgenus, R' is a hydrocarbon radical of valence x. R' may therefore be alkyl, cycloalkyl, aryl or aralkyl, and may be saturated or unsaturated, e. g., it may be methyl, ethyl, isopropyl, allyl, butyl, isobutyl, crotyl, hexyl, octyl, decyl, octadecyl, cyclopentyl, cyclohexyl, phenyl, tolyl naphthyl, tetrahydronaphthyl, benzyl, phenylethyl, ethylene, trimethylene, tetramethylene, decamethylene, m-phenylene, o- and p-xylylene. R' may also contain a hetero atom within the hydrocarbon chain, that is, R' may be heteroaliphatic or heterocyclic, e. g., ethoxyethyl, $-CH_2CH_2OC_2H_5$, propoxyethyl,

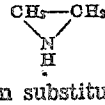
$$-CH_2CH_2OC_3H_7$$

(thioethyl) ethyl, $-CH_2CH_2SC_2H_5$, diethyl sulfide, $-CH_2CH_2SCH_2CH_2-$, diethyl oxide,

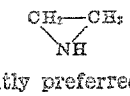
$$-CH_2CH_2OCH_2CH_2-$$

thienyl, pyrrolyl, pyridyl, piperidyl, quinolyl, etc.

The invention is generic to the use of ethylenimines, i. e., ethylenimine



and its hydrocarbon substitution products, e. g., those wherein the hydrogen on the nitrogen is replaced by methyl, ethyl, propyl, butyl, isobutyl, hexyl, decyl, dodecyl, hexadecyl, cyclohexyl, phenyl, benzyl, etc., and those wherein one or more hydrogens attached to the ethylenimine carbon are replaced by methyl, ethyl, butyl, hexyl, dodecyl, octadecyl, cyclohexyl, phenyl, etc. radicals. In the claims, when the term "an ethylenimine" is used, it is to be understood as including not only ethylenimine but also its hydrocarbon substitution products. The term "ethylenimine" in the singular without the indefinite article is meant to include only ethylenimine



which is the greatly preferred species, owing to its ready availability and ease of reaction.

The reaction temperature may be varied from slightly elevated temperature (e. g. 50° C.) to high temperature (e. g., 200° C.), the reaction time being, of course, reduced at the more elevated temperatures. Obviously, the temperature must be chosen so as to avoid decomposition of the starting materials or end product. In general, a temperature between 100° C. and 150° C. will be sufficient to bring about substantially complete reaction in a period of from 8 to 24 hours.

The reaction may be carried out either at atmospheric pressure or at superatmospheric pressure (in a closed vessel). The latter conditions are desirable when either the thiol or the ethylenimine or both are low boiling, in which case the reaction temperature in an open vessel would of necessity be low, with consequent increase of reaction time, and possibility of loss of reactants through evaporation. The pressure developed during the reaction will, of course, depend on the volatility of the reactants and on the temperature of the reaction, and the material of which the reactor is built will have to be chosen accordingly. When both reactants are sufficiently high boiling, the reaction may conveniently be carried out in an open vessel, with suitable provision for returning the condensed vapors to the reaction mixture.

The presence of a solvent is not necessary to the conduct of the operation. However, a solvent may be desirable in certain cases, for example, when the thiol to be reacted is a high melting solid. Any solvent which is inert towards both the thiol and the ethylenimine under the conditions of the reaction may be used, for example, aliphatic, cycloaliphatic, and aromatic hydrocarbons, ethers such as di-n-butyl ether, or cyclic ethers such as dioxane.

In general, catalysts are unnecessary as the reaction proceeds without a catalyst at appropriate temperature with sufficient speed. Acidic and basic materials used as catalysts in other reactions are in general to be avoided because, by catalyzing undesired side reactions, they decrease the yield and increase the difficulties of preparation. Thus, hexadecanthiol and ethylenimine in the presence of aqueous sodium hydroxide yield an apparently polymeric material of indefinite composition. Acidic conditions tend to polymerize the ethylenimine so that acidic catalysts are to be avoided.

The reaction products, i. e., the beta-aminoethyl sulfides, may be readily isolated and purified by the well-known methods which include, according to expediency, distillation, preferably under reduced pressure, crystallization, from solution or from a melt, steam distillation, etc. There is, in general, no difficulty in isolating the desired product in good yield, since little or no by-product or elimination product is formed in the process of this invention. In many cases the product may be used as such, without any purification.

It is, in general, advantageous to use the reactants (thiol and the ethylenimine) in molecular proportions, that is, one mol of the ethylenimine for each mercapto group. However, if desired, an excess of either reactant may be used. For example, it may be advantageous to use an excess of the more volatile, or of the cheaper, reactant if the reaction is carried out at atmospheric pressure.

The beta-aminoethyl sulfides produced according to the process of this invention are particularly valuable as anti-corrosion and anti-sludge agents in lubricating oils. They are also of great interest as starting materials in chemical syntheses, owing to the reactivity of the amino group. In these applications, the poly-(beta-aminoethyl) sulfides obtainable by the process of this invention are of particular interest In lubricating oil stabilizers of the beta-aminoethyl sulfide type, it is believed that the group

—S—CH_2—CH_2—NH_2 is responsible for the activity of the molecule as a whole. It is therefore advantageous to have more than one such group in the molecule. From another standpoint, and also by reason of their poly-functional character, the poly-(beta-aminoethyl) sulfides are useful ingredients in condensation and addition reactions, yielding valuable high molecular weight polymeric materials.

This invention is of advantage in making readily available certain hitherto difficultly obtainable beta-aminoethyl sulfides. A convenient route to the beta-aminoethyl sulfides is opened by this invention. The process herein disclosed is particularly easy to carry out, requiring no special or expensive equipment and a minimum of attention. It is further extremely advantageous in that no by-product is eliminated or evolved, thereby insuring easy isolation and purification of the final product. It is of further advantage in providing a means for the preparation of a new class of compounds hitherto unavailable, i. e., amine sulfides having a plurality of beta-aminoethylthio groups.

The above description and examples are intended to be illustrative only. Any modification of or variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

What is claimed is:

1. 1,6-bis(beta-aminoethylthio) hexane.

2. The process which comprises reacting, under 200° C. under substantially neutral conditions an ethylenimine and a thiol free from groups, other than thiol, reactive with the ethylenimine.

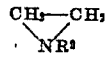
3. The process which comprises reacting at 50–200° C. under substantially neutral condition an ethylenimine and a thiol wherein the non-thiol portion of the molecule is selected from the class consisting of hydrocarbon radicals and hydrocarbon radicals containing a hetero atom in the carbon chain.

4. The process which comprises reacting at 50–200° C. under substantially neutral conditions an ethylenimine and a polythiol wherein the non-thiol portion of the molecule is selected from the class consisting of hydrocarbon radicals and hydrocarbon radicals containing a hetero atom in the carbon chain.

5. The process which comprises reacting at 50–200° C. under substantially neutral conditions ethylenimine and a thiol wherein the non-thiol portion of the molecule is selected from the class consisting of hydrocarbon radicals and hydrocarbon radicals containing a hetero atom in the carbon chain.

6. The process which comprises reacting at 50–200° C. under substantially neutral conditions ethylenimine and a polythiol wherein the non-thiol portion of the molecule is selected from the class consisting of hydrocarbon radicals and hydrocarbon radicals containing a hetero atom in the carbon chain.

7. A process comprising reacting under substantially neutral conditions at 50–200° C. a thiol $R'(SH)_x$, wherein R' is a hydrocarbon radical of valence x and x is an integer at least equal to 1, with an ethylenimine



wherein R^2 is a member of the class consisting of hydrogen and hydrocarbon radicals.

8. Process which comprises reacting, under substantially neutral conditions at 50–200° C., an ethylenimine with an alkanethiol.

9. Process which comprises reacting, under substantially neutral conditions at 50–200° C., ethylenimine with an alkanethiol.

10. Process which comprises reacting, under substantially neutral conditions at 50–200° C., an ethylenimine with an alkanepolythiol.

11. Process which comprises reacting, under substantially neutral conditions at 50–200° C., ethylenimine with an alkanepolythiol.

12. Process which comprises reacting ethylenimine with n-propanethiol under substantially neutral conditions at 50–200° C.

13. Process which comprises reacting ethylenimine with hexan-1,6-dithiol under substantially neutral conditions at 50–200° C.

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