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PROCESS OF PREPARING DERIVATIVES OF ETHYLENEIMINE

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The present invention relates to a process of preparing nitrogenous compounds which consists in attaching alpha,beta-alkylene imines, in the presence of alkali metals, to hydrocarbons having conjugated double bonds.

Furthermore, the present invention relates to some new compounds which are obtainable by the process described herein.

As alpha,beta-alkylene imines there may, for instance, be used: ethylene-imine, 1,2-propylene-imine, 1,1-dimethyl-ethylene-imine or other 1,2-alkylene imines possessing a hydrogen atom on the nitrogen atom.

Butadiene, isoprene, vinylbenzene, divinylbenzene, vinylnaphthalene, cyclo-octatetraene and others may be named, by way of example, as compounds having conjugated carbon double bonds.

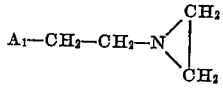
An especially suitable alkali metal is metallic sodium which is added in catalytic amounts to the alkylene imine. The other alkali metals, for instance, lithium and potassium, may also be used.

The use of indifferent solvents or diluents may be of advantage in the case of especially reactive diene compounds.

According to the present invention addition compounds of alpha,beta-alkylene imines and hydrocarbons having conjugated double bonds are obtained. The latter may be represented by the following general formula:

$$A—CH=CH_2$$

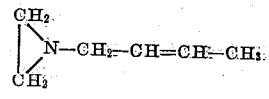
wherein A represents an organic radical which contains at least one double bond being in conjugated position to the double bond indicated above. Depending on the organic radicals which are present, the position of the added groups may vary. In the case of styrene and vinylnaphthalene, the nitrogen-containing group is fixed on the omega-carbon atom and there are obtained, for instance, compounds of the formula

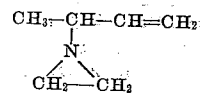


wherein A_1 stands for the phenyl or naphthyl radical. In other cases a shifting of the double bond may occur. From butadiene and ethylene

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imine a mixture of the following isomeric compounds is, for instance, obtained:





The products of the present invention are compounds of high reactivity. Owing to the ethylene imine ring contained in these compounds, they may be converted, with the aid of catalysts, into polymerization products. They serve as intermediate products or as auxiliaries in the textile and plastics industries.

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

Example 1

3 parts of sodium, cut into thin slices, are introduced into 258 parts of anhydrous ethylene imine. 312 parts of styrene are slowly added thereto, while stirring, and starting at a temperature of 25° C. When about 50 parts of styrene have been run in within about 10 minutes, the solution begins to assume a violet color and the addition reaction spontaneously sets in with ebullition of the ethylene imine. The further reaction takes place in a moderate manner according to the rate of running in the styrene. The catalytically acting sodium metal coheres to form a silvery ball on the setting in of the addition reaction. By external cooling the temperature is kept at 40–45° C. When the total amount of styrene has been run in, stirring is continued for 5 hours at room temperature. At the end of that period the liquid has a red color. It is separated from the undissolved sodium and distilled. 2.5 parts of unaltered sodium are recovered.

During the distillation at first the excess of ethylene imine is recovered. By a fractional distillation of the liquid addition product there is obtained, after a small portion of first runnings chiefly consisting of unaltered styrene, the N-(beta-phenylethyl)-ethylene imine boiling at 89° C. under a pressure of 6 mm. of mercury in a yield of 391 parts, i. e. 89 per cent. of the theoretical.

N-(beta-phenylethyl)-ethylene imine is a limpid, readily mobile liquid of penetrating odor.

Example 2

2 parts of sodium cut into slices are introduced into 86 parts of anhydrous ethylene imine. 54 parts of butadiene are slowly added thereto, while stirring. Soon after the introduction of the butadiene has begun, the addition reaction sets in and, after the first violent reaction, it proceeds uniformly. The temperature is kept at 30° C. by external cooling. On the setting in of the reaction, the sodium coheres to form a silvery ball. As soon as the introduction of butadiene has terminated, the evolution of heat ceases. Stirring is continued for 2 hours, and the reaction liquid is then separated from the unaltered sodium metal. After the distillation of the excess of ethylene imine, the N-butenyl-ethylene imine formed distils in a good yield in the form of a mixture of isomers boiling between 108° C. and 115° C. under a pressure of 760 mm. of mercury.

Example 3

1 part of sodium, cut into thin slices, is introduced into 30 parts of 1.2-propylene imine. 52 parts of styrene are slowly added thereto, while stirring. The temperature rises, first slowly, then rapidly to 60–70° C., where it is kept. The reaction heat is dissipated by carefully cooling with warm water. At the end of the reaction the mixture is heated for ¼ hour to 100° C. After cooling, the brown reaction liquid is separated from non-consumed sodium and subjected to a fractional distillation in a column under reduced pressure. The unaltered styrene distils as first runnings. The N-(beta-phenylethyl)-1.2-propylene imine formed distils at 82° C. at 23 Torr in the form of a liquid readily soluble in dilute acid. The yield amounts to 50 parts.

I claim:

1. The process which comprises reacting, in the presence of alkali metals, ethylene imine with a hydrocarbon selected from the group consisting of butadiene and styrene.

2. The process which comprises reacting, in the presence of alkali metals, ethylene imine with butadiene.

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