United States Patent Office 2,903,482 Patented Sept. 8, 1959

2,903,482

PRODUCTION OF OXIMES

Heinrich Hopff, Zurich, Switzerland, and Otto von Schickh and Hans-Joachim Riedl, Ludwigshafen (Rhine), Germany, assignors to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany

No Drawing. Application June 16, 1953
Serial No. 362,124

Claims priority, application Germany July 19, 1952

11 Claims. (Cl. 260—566)

This invention relates to an improved process for the production of oximes by reduction of aliphatic or cycloaliphatic secondary nitro compounds.

We have found that oximes are obtained in good yields by reacting secondary aliphatic or cycloaliphatic nitro compounds in the form of their salts or in the free aci-form with thiosulfuric acid or its salts in an acid medium.

Suitable nitro compounds are for example 2-nitropropane, nitrocyclohexane, nitrocyclo-pentane, methylated nitrocyclohexanes, the secondary nitrobutanes and -hexanes. They are preferably used in the form of their alkali, alkaline earth or ammonium salts or free aci-forms. It is supposed that the free aci-forms are intermediates of the process. The thiosulfuric acid is also preferably used in the form of its alkali or ammonium salts.

The procedure may be for example that aqueous solutions of about equivalent amounts of said salts of the nitro-compounds and of thiosulfuric acid are stirred either after previous mixing or simultaneously but separately into dilute acids. Suitable acids are for example sulfuric acid, phosphoric acid, hydrochloric acid or para-toluene sulfonic acid. If desired, inert organic solvents or dispersing agents can also be co-employed.

Instead of using thiosulfuric acid or its salts, there may also be used for the process compounds from which thiosulfuric acid or its salts can form in known manner. Such mixtures consist for example of about equivalent amounts of water-soluble sulfites and sulfur, of sulfides and sulfur dioxide, of sulfides and polythionates, or of polythionates and alkalies.

The said mixtures may be first converted in known manner into thiosulfuric acid or its salts and then added to the aci-nitro compounds or their salts; the formation of the thiosulfuric acid salts may, however, also be allowed to take place in the presence of the salts of the nitro compounds. In any case the conversion of the nitro compounds into the desired oximes is effected by bringing the whole mixture to an acid pH-value or by maintaining the same by the continuous or periodic addition of, for example, mineral acid.

The reaction generally takes place very rapidly even at room temperature. The process can therefore very readily be carried out continuously by allowing the solutions of the salts of the nitro compounds and of thiosulfuric acid to flow together with excess acid for example in a mixing tube.

It is also possible to work while cooling or at raised temperatures if necessary.

The reaction mixture must in all cases be acid, but the exact pH-value is not important. Thus an excess of acid may be present from the start or care may be taken by the occasional or continuous addition of acid that the reaction mixture is always acid.

The process can be rendered especially advantageous if the mother liquors remaining from the reduction of

the nitro compounds with thiosulfuric acid or its salts after complete or partial separation of the oximes formed are regenerated by known methods to thiosulfuric acid or its salts and these are used again for the reaction with the nitro compounds. It has been found that by reaction with the nitro compounds the thiosulfuric acid or its salts is oxidised to polythionic acids, in particular tetrathionic acid, or their salts. For the regeneration of the mother liquor, therefore, they are treated by known methods by which polythionic acids or their salts are converted into thiosulfuric acid or its salts.

The mother liquor may be reduced for example with alkali sulfides or with alkali amalgams, as for example the technical amalgams obtained by the electrolysis of alkali chlorides. The necessary amount of these reducing agents can be readily calculated or ascertained by preliminary experiments. Upon repeated regeneration, the mother liquor becomes enriched with a large amount of the indifferent salt simultaneously formed, as for example sodium sulfate, which finally crystallises out and can then easily be removed by filtration or by suction.

In this way any large amount of nitro compound can be converted into the corresponding oxime by means of a relatively small amount of thiosulfate which is continually regenerated. This embodiment of the process can also readily be rendered continuous.

The mother liquors containing polythionates can also be regenerated by other usual processes. For example if they are boiled with alkali carbonates or earth alkaline hydroxides, there are obtained, as already known, 7 mols of thiosulfate from 4 mols of tetrathionate. The mother liquors can also be heated without any addition of alkali, whereby the polythionate decomposes into sulfur dioxide, free sulfur and sulfate; the sulfur dioxide and sulfur can then be reacted to thiosulfate by the usual methods.

Various embodiments of the process according to this invention are illustrated by the following examples but the invention is not limited thereto. The parts are parts by weight.

Example 1

A solution of 248 parts of crystallised sodium thiosulfate in 150 parts of water is added to a solution of 64.5 parts of nitrocyclohexane in 235 parts of 9% caustic soda solution. The mixture is allowed to flow into 900 parts of 2-normal sulfuric acid while stirring vigorously at about 20° C. Cyclohexanone oxime begins to crystallise out even before the end of the introduction. The reaction mixture, permeated with crystals, is neutralised with sodium carbonate solution and the oxime then filtered off by suction. Further oxime is recovered from the mother liquor by extracting with, for example, ether. The total yield amounts to 50 to 52 parts corresponding to about 90% of the theoretical yield.

Example 2

252 parts of crystallised sodium sulfite, 32 parts of sulfur powder and 200 parts of water are added to a solution of 64.5 parts of nitrocyclohexane in 235 parts of 9% caustic soda solution, and the mixture is shaken at room temperature until the sulfur has dissolved completely. The solution, containing now sodium thiosulfate, after filtration if necessary, is then allowed to flow at about 20° C. into 900 parts of 2-normal sulfuric acid while stirring vigorously. A considerable part of the cyclohexanone oxime formed is thus crystallised out. Further amounts of oxime can be recovered from the filtrate by extraction, for example with ether. The total yield is 50 to 52 parts of pure cyclohexanone oxime, corresponding to about 90% of the theoretical yield calculated on the nitrocyclohexane used.

Example 3

A solution of 120 parts of crystallised sodium sulfide in 150 parts of water is stirred gradually into a suspension of 151 parts of potassium tetrathionate in 150 parts of water, the temperature being kept at about 20° C. by cooling. The potassium tetrathionate passes into solution while free sulfur separates at the same time. The latter is filtered off, the filtrate containing now sodium thiosulfate is mixed with a solution of 64.5 parts of nitrocyclohexane in 235 parts of 9% caustic sodia solution and the mixture is stirred into 900 parts of 2-normal sulfuric acid as described in Example 2. About 52 parts of pure cyclohexanone oxime, corresponding to about 90% of the theoretical yield, are obtained.

Example 4

173 parts of potassium tetrathionate are boiled with a solution of 76 parts of anhydrous sodium carbonate in 240 parts of water for 2 to 3 hours under reflux, whereby potassium sulfate separates out and if desired can be filtered off. A solution of 64.5 parts of nitrocyclohexane in 235 parts of 9% caustic soda solution are then added at room temperature to the filtrate containing potassium thiosulfate and the whole is allowed to flow into 900 parts of 2-normal sulfuric acid as described in Example 2. The yield of pure cyclohexanone oxime is 47 to 49 parts, corresponding to about 85% of the theoretical yield.

Example 5

64.5 parts of nitrocyclohexane are dissolved in 235 parts of 9% caustic soda solution, a solution of 248 parts of crystallised sodium thiosulfate in 150 parts of water is added and the whole is stirred into 900 parts of 2-normal sulfuric acid at about 20° C. The reaction mixture, permeated with crystals of cyclohexanone oxime, is neutralised with alkali carbonate, whereupon the oxime is separated. While cooling and stirring the filtrate, there is added a solution of 120 parts of crystallised sodium sulfide in 150 parts of water. The precipitated sulfur is filtered off by suction and the solution containing now regenerated sodium thiosulfate is concentrated to about its original volume. Then, if necessary after filtering off by suction any sodium sulfate which has crystallised out, there is added a solution of another 64.5 parts of nitrocyclohexane in 235 parts of 9% caustic soda solution and the whole is again allowed to flow at about 20° C. into 900 parts of 2-normal sulfuric acid while stirring, and the procedure described above is repeated. The yield of pure cyclohexanone oxime is on an average 85 to 90% of the theoretical yield (with reference to nitrocyclohexane used) even after frequent repetition of the sequence of reactions.

Example 6

A solution of 1042 parts of crystalline sodium thiosulfate in 630 parts of water is combined with a solution of 258 parts of nitrocyclohexane in 940 parts of 9 percent caustic soda solution. The mixture is then poured all at once into a well cooled mixture of 547 parts of 19.5–n sulfuric acid and 600 parts of ice with vigorous agitation, cyclohexanone oxime crystallising out after a short time. The reaction mixture is neutralised with sodium carbonate and the oxime is filtered off by suction. It is obtained with a yield of 200 to 204 parts which amounts to about 90 percent of the theoretical yield.

The mother liquor is boiled with 222 parts of calcium hydroxide for 2 to 3 hours with agitation, the calcium sulfate formed is stripped by filtration and the filtrate containing now regenerated sodium thiosulfate is mixed with a solution of 193.5 parts of nitrocyclohexane in 705 parts of 9 percent caustic soda solution. This mixture is poured into a mixture of 404 parts of 19.5–n sulfuric acid and 720 parts of ice with vigorous agitation. After neutralising with sodium carbonate the cyclohexanoneoxime is filtered off by suction. By shaking out with ether further oxime is obtained. The total yield is about 150 to 152 parts which amounts to about 90 percent of the theoretical yield.

When boiling the mother liquor with 400 parts of calcium carbonate, instead of with 222 parts of calcium hydroxide as aforesaid, filtering, adding a solution of 168 parts of nitrocyclohexane in 611 parts of 9 percent caustic soda solution, pouring the mixture into a mixture of 640 parts of ice and 355 parts of 19.5–n sulfuric acid with agitation and further processing as described in the previous paragraph of this example, there are obtained 130 to 132 parts of cyclohexanoneoxime which corresponds to a yield of about 90 percent of the theoretical yield.

Example 7

A solution of 258 parts of nitrocyclohexane in 940 parts of 9 percent caustic soda solution is combined with a solution of 1042 parts of crystalline sodium thiosulfate in 1330 parts of water, the mixture is cooled to —11° C. with agitation and a mixture, cooled to —11° C., of 356 parts of 96% sulfuric acid and 100 parts of water is run in all at once while cooling, with agitation. After about 5 minutes the whole is neutralised without cooling with a sufficient quantity of anhydrous sodium carbonate and then heated to about 26° C. The cyclohexanoneoxime formed is filtered off by suction and washed with some water. The yield is 204 parts which amounts to 90% of the theoretical yield.

The mother liquor is combined with 222 parts of calcium hydroxide and then heated at ordinary pressure while stirring until 650 parts of an aqueous distillate have passed over. From this distillate 11 to 15 parts of cyclohexanone can be isolated. 48 parts of sulfur and 10 parts of crystalline sodium sulfide are added to the distillation residue and the mixture is boiled under reflux for 6 hours with vigorous agitation. The precipitate and the supernatant liquid are separated by suction, the precipitate then being washed with 400 parts of water. To the aqueous filtrates, while being heated, are added sodium carbonate to the extent that the dissolved calcium completely settles out as carbonate. The mixture is then cooled down to about 0° C., while stirring, whereby also the major portion of the sodium sulfate precipitates. The whole precipitate is filtered off by suction and washed with some water. The thiosulfate contents of the aqueous filtrate is determined in the usual manner.

The amount of aqueous filtrates that corresponds to a crystalline sodium thiosulfate content of 1042 parts is combined, while stirring, with a solution of 85 parts of sodium hydroxide in 85 parts of water and with 258 parts of nitrocyclohexane. When the latter has dissolved, the solution is diluted to about the same volume as in the first paragraph of this example, cooled down to —11° C. and reacted with sulfuric acid as described above, 200 to 204 more parts of cyclohexanoneoxime being thus obtained.

The mother liquor can again be regenerated and reused as described above. Even if the process described in the second paragraph of this example will be repeated a plurality of times, equal amounts of cyclohexanoneoxime of equal quality are obtained.

Example 8

Through a coil, about 6 centimeters in diameter, made of a tube of stainless steel of about 10 meters in length and 4 millimeters in internal width, are simultaneous passed, in the course of 3 minutes, a solution, cooled down to 5° C., of 258 parts of nitrocyclohexane in 940 parts of 9% caustic soda solution, to which a solution of 1042 parts of crystalline sodium thiosulfate in 1330 parts of water which has likewise been cooled has been added, as well as a mixture, likewise cooled to 5° C., of 356 parts of 96% sulfuric acid and 100 parts of water. The

coil is cooled from outside by running water so that the reaction mixture leaves at a temperature of about 20° C. The reaction mixture is neutralised with anhydrous sodium carbonate, heated to about 26° C. and the cyclohexaneoxime is filtered off by suction. The yield amounts to about 192 parts corresponding to 85% of the theoretical yield.

The dimensions of the tube may vary within wide limits, but should desirably be such that turbulence is set up in the tube.

The neutralisation and suction can also be practiced in a continuous manner.

Example 9

A solution of 1042 parts of crystalline sodium thiosulfate in 1330 parts of water is added to a solution of 178 parts of 2-nitropropane in 940 parts of 9% caustic soda solution and then, after cooling the mixture to −11° C., a mixture of 356 parts of 96% sulfuric acid and 100 parts of water which has been cooled to −10° C. is run in at a fast rate while cooling intensely and stirring vigorously. After about 5 minutes the reaction mixture is neutralised without further cooling by adding sodium carbonate in portions, and then heated to about 26° C. It is then exhaustively extracted with ether. The ethereal extract is dried with sodium sulfate, filtered and stripped of ether in a high-efficiency column. By distillation at atmospheric pressure there are obtained about 132 parts of acetone oxime (B.P. 130°–136° C.), i.e. 90% of the theoretical yield.

Example 10

A mixture of 178 parts of 2-nitropropane, 78 parts of calcium hydroxide and 880 parts of water is stirred at ambient temperature until all of the 2-nitropropane has dissolved. The mixture is then filtered and the filtrate is combined with a solution of 1040 parts of crystalline calcium thiosulfate in 800 parts of water. The whole is then entered in the course of a few minutes into 3520 parts of 2–n hydrochloric acid while stirring and cooling down to about 20° C. After standing for 5 minutes the mixture is neutralised with calcium hydroxide and extracted with ether. When further processing as described in Example 9 there are obtained about 124 parts of acetone oxime, i.e. 85 percent of the theoretical yield.

Example 11

A solution of 248 parts of crystalline sodium thiosulfate in 150 parts of water is added to a solution of 58.5 parts of 3-nitropentane in 235 parts of 9% caustic soda solution. The mixture, while being vigorously stirred and intensely cooled, is run into 900 parts of 2–n sulfuric acid at about 20° C. Then the whole is neutralised with sodium carbonate, extracted with ether and further processed as described in Example 9. There are obtained about 41 parts of diethylketoneoxime (B.P. 165%), i.e. 80% of the theoretical yield.

Example 12

57.5 parts of nitrocyclopentane are stirred with 200 parts of an about 12–n aqueous ammonia solution until a clear solution is obtained. When this has occurred after about 2 hours stirring, a solution of 156 parts of ammonium thiosulfate in 160 parts of water is added and the whole is run at a fast rate, with vigorous agitation, into a freshly prepared mixture of 1800 parts of pounded ice and 188 parts of 96% sulfuric acid. After 5 minutes standing the whole is neutralised with concentrated ammonia solution and the cyclopentanone oxime formed is obtained by extraction with ether, drying the ethereal extract and evaporating the ether. There are obtained 42 parts of cyclopentanoneoxime (M.P. 56° C.), i.e. 85% of the theoretical yield.

Example 13

A solution of 286 parts of 1-methyl-3-nitrocyclohexane in 940 parts of 9% caustic soda solution is combined with a solution of 1040 parts of crystalline sodium thiosulfate in 1330 parts of water. The mixture is cooled down to −11° C.; then is entered at a fast rate, with vigorous agitation and intense cooling, a mixture of 356 parts of 96% sulfuric acid and 100 parts of water which has been cooled to −10° C. When further processing as described in Example 9 a viscous oil is obtained which consists of the oxime of 1-methylcyclohexanone-(3) and boils at between 110° and 116° C. at a pressure of 15 millimeters (mercury gauge). The yield is about 202 parts, i.e. 80% of the theoretical yield.

What we claim is:

1. A process for the production of cyclohexanone oxime which comprises introducing a solution of nitrocyclohexane in aqueous sodium hydroxide containing about equivalent amounts of sodium thiosulfate into excess aqueous sulfuric acid.

2. A process for the production of cyclohexanone oxime which comprises passing simultaneously and turbulently through a tubular reaction zone excess mineral acid and a solution of nitrocyclohexane in aqueous alkali hydroxide containing about equivalent amounts of alkali thiosulfate.

3. A process for the production of cyclopentanone oxime which comprises diluting nitrocyclopentane in an aqueous ammonia solution, adding about equivalent amounts of ammonium thiosulfate and introducing the mixture into excess sulfuric acid.

4. A process for the production of 1-methyl-3-cyclohexanone oxime which comprises introducing a solution of 1-methyl-3-nitrocyclohexane in an aqueous caustic soda solution containing about equivalent amounts of sodium thiosulfate into excess sulfuric acid.

5. A process for the production of acetone oxime which comprises stirring a mixture of 2-nitropropane, calcium hydroxide and water until all of the 2-nitropropane has dissolved, adding about equivalent amounts of calcium thiosulfate and introducing the mixture into excess hydrochloric acid.

6. A process for the production of diethyl ketone oxime which comprises introducing a solution of 3-nitropentane in aqueous sodium hydroxide solution containing about equivalent amounts of sodium thiosulfate into excess sulfuric acid.

7. A process for the preparation of cyclohexanoneoxime which comprises reducing an alkali metal salt of nitrocyclohexane with an equivalent amount of an alkali metal thiosulfate in an aqueous medium in the presence of excess mineral acid.

8. A process for the production of ketoximes which comprises reacting a member of the group consisting of the alkali metal, alkaline earth metal and ammonium salts of the 2-nitropropane, secondary nitrobutane, nitropentane, and nitrohexane, nitrocyclohexane, methyl nitrocyclohexane and nitrocyclopentane with thiosulfuric acid in a mineral acid medium.

9. A process for the production of ketoximes which comprises reacting a member of the group consisting of the alkali metal, alkaline earth metal and ammonium salts of the 2-nitropropane, secondary nitrobutane, nitropentane, and nitrohexane, nitrocyclohexane, methyl nitrocyclohexane and nitrocyclopentane with thiosulfuric acid at from about −11° to about +20° C. in a mineral acid medium.

10. A process for the production of ketoximes which comprises introducing an aqueous solution containing about equivalent amounts of a member of the group consisting of the alkali metal, alkaline earth metal and ammonium salts of the 2-nitropropane, secondary nitrobutane, nitropentane, and nitrohexane, nitrocyclohexane, methyl nitrocyclohexane and nitrocyclopentane, and of a member of the group consisting of the alkali metal, alkaline earth metal and ammonium salts of thiosulfuric acid at from about −11° to about +20° C. into excess mineral acid.

11. A process for the production of ketoximes which comprises introducing excess mineral acid at from about —11° to about +20° C. into an aqueous solution containing about equivalent amounts of a member of the group consisting of the alkali metal, alkaline earth metal and ammonium salts of the 2-nitropropane, secondary nitrobutane, nitropentane, and nitrohexane, nitrocyclohexane, methyl nitrocyclohexane and nitrocyclopentane, and of a member of the group consisting of the alkali metal, alkaline earth metal and ammonium salts of thiosulfuric acid.

References Cited in the file of this patent

FOREIGN PATENTS

171,709 Austria ---------- June 25, 1952

OTHER REFERENCES

Chemical Abstract, vol. 35, column 3985 (1941).