

## UNITED STATES PATENT OFFICE

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## PREPARATION OF ORGANIC THIOCYANATES

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The present invention relates to the production of organic thiocyanates and more particularly to an improved method for such production.

An object of the present invention is to provide a method for producing such thiocyanates whereby they may be obtained in high yields and at low cost.

A further object of the present invention is to provide an improved method whereby a mercaptan may be converted to the corresponding thiocyanate.

A still further object is to provide a method whereby a mercaptan may be converted to the corresponding thiocyanate without the necessity of going through the preparation and isolation of a mercaptide.

Other objects of the invention will be made apparent from the discussion hereinafter.

In the past, organic thiocyanates have been provided in small quantities and by expensive methods which include reaction of alkyl or acyl halides or dialkyl sulfates with inorganic thiocyanates, the addition of thiocyanic acid to olefins or ethylene oxide, the addition of thiocyanogen to olefins to produce dithiocyanates, the action of potassium and copper thiocyanates on aromatic diazonium salts, and the reaction of a mercaptide with cyanogen chloride. Of these methods the most widely used has been the reaction between an alkyl or acyl halide or dialkyl sulfate with an inorganic thiocyanate. However, this general method involves a laborious procedure which provides the desired thiocyanates in low yield and at high cost. Inasmuch as a large number of mercaptans have recently been made available on a commercial scale by their isolation from petroleum products, a method whereby such mercaptans could be used in the preparation of organic thiocyanates is highly desirable. As indicated hereinabove, mercaptans previously employed in the preparation of thiocyanates have first been converted to mercaptides. Specifically, the prior art shows that the lead salts of the allyl, phenyl, and substituted phenyl mercaptans have been reacted with cyanogen chloride to give the corresponding thiocyanates in unspecified yields. In attempts to duplicate this work using various other lead mercaptides, it has been found that this method leaves much to be desired. Particularly difficult and laborious is the preparation and isolation of the lead or other metal mercaptides.

It has now been discovered that mercaptans may be directly converted to the corresponding thiocyanates by treatment with a cyanogen halide

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without the necessity of first preparing the mercaptides, such as the lead or mercury mercaptides, provided that a hydrogen halide acceptor is present in the reaction mixture. Such acceptors are the strong bases such as the alkali metal and alkaline earth metal oxides, hydroxides and alkoxides and are best employed in equivalent quantities. It has been stated that the mercaptans may be converted to the corresponding thiocyanates by treatment with a cyanogen halide implying that this may be done without the necessity of going through the formation of the mercaptides. However, this method for preparing organic thiocyanates requires long periods of reaction and results in very low yields so that it is understandable why in the past it has been deemed advisable to proceed through the troublesome preparation of the mercaptide in order to obtain reasonable yields of the desired thiocyanates. The method of the present invention thus retains the advantage of being able to proceed directly from the mercaptan to the corresponding thiocyanate while providing high yields of the desired thiocyanates using short periods of reaction.

While the reaction may be carried out in a large number of solvents or diluents such as esters, ketones, ethers, alcohols, aromatic and aliphatic hydrocarbons, and the like, it is preferred to employ those in which the acceptor such as the alkali metal and alkaline earth metal oxides, hydroxides and alkoxides is substantially insoluble. The use of a medium in which the acceptor has an appreciable solubility results in the formation of the organic sulfide, or thioether, corresponding to the mercaptan reactant, whereas the use of a medium in which the acceptor is substantially insoluble results in a minimum of sulfide formation. Thus, the hydrocarbons, such as pentane, hexane, heptane, and other petroleum fractions and benzene, toluene, the xylenes, ethyl benzene and the like are preferred, the aliphatic hydrocarbons being more preferable.

While any of the cyanogen halides may be employed in the present invention and may be added per se or dissolved and/or diluted in suitable liquids, it is preferred that they be added in the latter form. Further, in the case of cyanogen chloride which is usually employed because of its greater availability, the cyanogen halide is preferably introduced into the reaction zone in vapor form. Such vapor may be added by introducing the gas above or below the level of the reaction mixture.

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While a wide range of temperatures may be employed for the reaction, lower temperatures are preferred since their use generally results in higher yields by minimizing side reactions such as those which result in sulfide formation, temperatures within the range of 0°–50° C. being preferred and those within the range of 0°–20° C. being still more preferable.

The isocyanates of the present invention are particularly useful as insecticides and have additional uses as chemical intermediates in the preparation of a large number of compounds such as acyl dithiocarbamates, aliphatic sulfonyl halides, imido thiol esters, thiourethanes, and the like.

The following examples are provided as illustrative of the present invention and should not be construed as limiting the scope of the invention in any manner, said scope being determined solely in the light of the appended claims.

## EXAMPLE 1

*n-Octyl thiocyanate*

(A) 4.6 g. of metallic sodium were dissolved in 100 ml. of absolute ethanol and 29.2 g. of *n*-octyl mercaptan were then added. The solution was heated to 30° C. and the addition of 12.5 ml. of cyanogen chloride was begun. Such addition required 2 hours, the temperature rising as high as 45° C. The mixture was then heated under reflux at 60°–65° C. for 1 hour, cooled, and the sodium chloride was filtered. The alcohol was removed under reduced pressure and the residue was filtered from a small amount of gummy material. This oil was dissolved in benzene and the benzene solution was washed several times with 10% HCl, followed by washing with 10% NaOH, then with water, and drying. After removal of the benzene, distillation gave 11.0 g. (32% yield) of *n*-octyl thiocyanate, B. P. 140°–170° C./28 mm. and 10.0 g. (40% yield) of di-*n*-octyl sulfide, B. P. 150°–153° C./2 mm.

(B) 16.4 g. of NaOH were dissolved in 100 ml. of water and 58.4 g. of *n*-octyl mercaptan were added with stirring. Most of the mercaptan dissolved after a short period of stirring. The addition of 21 ml. of cyanogen chloride was begun and 2 hours were required for such addition. The mixture was cooled to 15° C., treated with 150 g. of ice and filtered to obtain 51 g. of an orange colored liquid. Said liquid was dissolved in benzene, washed with acid followed by alkali and water, and indicated under (A), and dried. Distillation gave 10.4 g. (15% yield) of crude *n*-octyl thiocyanate at 90°–110° C./2 mm. and 29 g. (56% yield) of di-*n*-octyl sulfide at 154°–160° C./2 mm. 3 g. of the *n*-octyl mercaptan were recovered.

(C) 16.0 g. of NaOH were suspended in 200 ml. of benzene and 58.4 g. of *n*-octyl mercaptan were added. The stirred mixture was cooled to 10° C. and the addition of 23 ml. of cyanogen chloride was begun. The addition of the cyanogen chloride required 1 hour and during this period the temperature was maintained at 9°–12° C. After the cyanogen chloride addition, the mixture was stirred at 10° C. for 30 minutes and for an additional 30 minutes without cooling during which time the temperature rose to room temperature. The reaction mixture was filtered, the benzene removed under reduced pressure and fractionation of the residue yielded 7.0 g. (12% recovery) of the mercaptan at 80°–96° C./4 mm., 31.0 g. (45% yield) of *n*-octyl thiocyanate at 96°–103° C./4 mm. and a small amount of di-*n*-octyl sulfide at 166°–176° C./4 mm.

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(D) In this experiment hexane was used to replace the benzene employed under (C) to still further decrease the solubility of the NaOH and thereby further curtail the extent of the side-reaction. In all other respects the conditions of the experiment were substantially identical to those employed under (C). However, a higher yield of *n*-octyl thiocyanate (56%) as compared with that provided under (C) was obtained.

## EXAMPLE 2

*Isopropyl thiocyanate*

(A) 16.0 g. of NaOH were suspended in 200 ml. of absolute ethanol with stirring and 30.4 g. of isopropyl mercaptan were added to the slurry at 25°–30° C. The resulting clear solution was cooled at 10° C. in an ice bath and the addition of 22 ml. of cyanogen chloride was begun. Said addition required 1 hour and the temperature was maintained at 10°–12° C. After stirring at 10° C. for 1 hour and at 10°–20° C. for an additional 30 minutes, the mixture was filtered and the filtrate was fractionated through a two-foot spiral column using a total reflux partial take-off still head. Fractionation yielded two lower boiling fractions and a higher boiling fraction amounting to 16.5 g., boiling at 148°–170° C. Redistillation of this latter fraction gave 4.5 g. (11% yield) of crude isopropyl thiocyanate at 148°–160° C. and 6.0 g. (20% yield) of diisopropyl sulfide at 169°–170° C.

(B) 16.0 g. of NaOH were suspended in 200 ml. of benzene and 30.4 g. of isopropyl mercaptan were added with stirring. The addition of 22 ml. of cyanogen chloride was begun and during the 1 hour required for said addition the temperature was maintained at 10°–15° C. After an additional hour of stirring at 15° C. the mixture was filtered, the solid retained on the filter paper was dissolved in 50 ml. of water and this solution extracted with 50 ml. of benzene. The benzene extraction was combined with the benzene filtrate and after drying over sodium sulfate, the benzene was removed under reduced pressure and the residue was fractionated through a two-foot spiral column. Said fractionation yielded 30.0 g. (75% yield) of isopropyl thiocyanate at 150°–152° C., the remainder being substantially unreacted isopropyl mercaptan and no appreciable amount of sulfide being obtained.

## EXAMPLE 3

*n-Butyl thiocyanate*

(A) 90.0 g. of *n*-butyl mercaptan were dissolved in 200 ml. of benzene and heated to 52° C. and the addition of 30 ml. of cyanogen chloride was begun. Said addition required 30 minutes during which time no appreciable temperature rise was experienced. The solution was then stirred at 40°–50° C. for 3 hours and at room temperature for 3 days. The mixture was filtered to remove about 3 g. of solid material and the benzene was removed under reduced pressure during which time copious fumes of HCl were evolved. Fractionation of the residue using a two-foot column yielded 28.5 g. (31% recovery) of the *n*-butyl mercaptan and 20.5 g. (30% yield) of *n*-butyl thiocyanate, B. P. 83° C./28 mm.

(B) 40.3 g. of powdered NaOH were suspended in 200 ml. of benzene and 90.0 g. of *n*-butyl mercaptan were added with stirring. The addition of 55 ml. of cyanogen chloride was begun after the benzene slurry was cooled to 10°–15° C. and required 40 minutes during which time a deep yellow color developed in the benzene solution.

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The mixture was stirred at 10° C. for 1 hour and the temperature was allowed to rise to room temperature while the mixture was stirred for an additional 30 minutes. The mixture was filtered, and after removing the benzene under reduced pressure the filtrate provided 71.5 g. (62% yield) of n-butyl thiocyanate at 78°–84° C./19 mm.

## EXAMPLE 4

*Tert-butyl thiocyanate*

25.5 g. of powdered KOH were slurried in 250 ml. of benzene and 41 g. of tert-butyl mercaptan were added and the mixture cooled to 5° C. in an ice bath. The addition of 21 ml. of cyanogen chloride which required 45 minutes was begun. The temperature was maintained at 5°–10° C. during this period and thereafter the mixture was stirred for an additional hour and at room temperature for another hour. The mixture was filtered and the precipitate washed with benzene. After removal of the benzene under reduced pressure, fractionation of the filtrate yielded 34 g. (75% yield) of colorless tert-butyl thiocyanate at 90° C./93 mm.

## EXAMPLE 5

*Tert-octyl thiocyanate*

(A) After dissolving 58.4 g. of mixed tert-octyl mercaptans (B. P. 59°–70° C./20 mm.) in 250 ml. of benzene, 16 g. of powdered NaOH were added with stirring. The mixture was cooled to 10° C. and 23 ml. of cyanogen chloride were added in 30 minutes. During the cyanogen chloride addition the temperature rose to 17° C. The mixture was stirred at 10° C. for 1 hour and at 10°–20° C. for 2 hours and filtered. The benzene was removed under reduced pressure and the residue was fractionated to yield 13.0 g. of low boiling material which was mainly mercaptan and 11.5 g. (17% yield) of mixed tert-octyl thiocyanates at 79°–84° C./5 mm.

(B) The experiment described under (A) was repeated except that in place of the NaOH 14.8 g. of  $\text{Ca}(\text{OH})_2$  was employed as the acceptor for the hydrogen chloride. After the removal of the benzene under reduced pressure, fractionation provided 10.2 g. (15% yield) of mixed tert-octyl thiocyanates at 60°–70° C./4 mm.

## EXAMPLE 6

*Tert-dodecyl thiocyanates*

60.6 g. of mixed tert-dodecyl mercaptans (B. P. 70°–80° C./5 mm.) were dissolved in 250 ml. of benzene and 12 g. of powdered NaOH were added with stirring. The stirring was continued for 30 minutes at 23°–29° C. and the mixture was then warmed to 60° C. and maintained at that temperature for 10 minutes and thereafter cooled to 13° C. 16 ml. of cyanogen chloride were added as a vapor over a period of 20 minutes while maintaining the temperature of the mixture at 13°–28° C. and thereafter the mixture was stirred at room temperature for an additional hour. The mixture was filtered, washed with water and dried over  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ . After removal of the benzene under reduced pressure, fractionation provided 11.0 g. (18% recovery) of the mixed tert-dodecyl mercaptans at 65°–85° C./5 mm. and 29.2 g. (44% yield) of mixed tert dodecyl thiocyanates at 85°–110° C./5 mm.

## EXAMPLE 7

*Allyl thiocyanate*

37.0 g. of allyl mercaptan were dissolved in 150 ml. of absolute ethyl ether, 20 g. of powdered

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NaOH were added and the mixture stirred at 25°–30° C. for 15 minutes. The mixture was then cooled to 3° C. and the addition of 20 ml. of cyanogen chloride in vapor form was begun. During this addition which required 1 hour the temperature rose to 11° C. The mixture was then stirred for an additional hour at 10°–20° C. and filtered. After drying the mixture overnight by treatment with "Drierite" ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) the ether was removed under reduced pressure and 8.0 g. of a mixture of allyl thiocyanate and allyl isothiocyanate was obtained at 148°–157° C./2 mm. Of this mixture 5.2 g was allyl thiocyanate.

## EXAMPLE 8

*Phenyl thiocyanate*

A suspension of 16 g. of NaOH in 200 ml. of benzene was prepared and 44 g. of thiophenol were added slowly. The mixture was then cooled to 5° C. and 20.3 ml. of cyanogen chloride in vapor form were added over a period of 1 hour while maintaining the temperature at 5°–10° C. The mixture was then stirred for an additional 2 hours at 125° C. and filtered to remove the precipitated NaCl which was washed with a little benzene. The filtrate was distilled under reduced pressure and after removal of the benzene 35 g. (65% of theory) of phenyl thiocyanate were obtained at 61°–66° C./2 mm.

In addition to the mercaptans employed in the foregoing examples other mercaptans which may be converted to the corresponding thiocyanates by the process of the present invention are the methyl, ethyl, n-propyl, furfuryl, isobutyl, sec-amyl, isoamyl, n-amyl, n-hexyl, thienyl, n-heptyl, benzyl, p-tolyl,  $\alpha$ -phenylethyl, n-nonyl, cetyl, biphenyl mercaptan and the like.

What is claimed is:

1. A process for preparing a hydrocarbon substituted thiocyanate which comprises reacting the corresponding mercaptan with a cyanogen halide in the presence of an equivalent weight of a member of the group consisting of the alkali metal and alkaline earth metal oxides, hydroxides and alkoxides in a liquid in which the members of said group are substantially insoluble.

2. A process for preparing a hydrocarbon substituted thiocyanate which comprises reacting the corresponding mercaptan with a cyanogen halide in the presence of an equivalent weight of a member of the group consisting of the alkali metal and alkaline earth metal oxides, hydroxides and alkoxides in a liquid hydrocarbon.

3. A process for preparing a hydrocarbon substituted thiocyanate which comprises reacting the corresponding mercaptan with cyanogen chloride in the presence of an equivalent weight of an alkali metal hydroxide in a liquid hydrocarbon.

4. A process for preparing a hydrocarbon substituted thiocyanate which comprises reacting the corresponding mercaptan with cyanogen chloride in vapor form in the presence of an equivalent weight of an alkali metal hydroxide in a liquid hydrocarbon.

5. A process for preparing a hydrocarbon substituted thiocyanate which comprises reacting the corresponding mercaptan with cyanogen chloride in vapor form in the presence of an equivalent weight of an alkali metal hydroxide in a liquid hydrocarbon within the temperature range of substantially 0°–50° C.

6. A process for preparing a hydrocarbon substituted thiocyanate which comprises reacting the corresponding mercaptan with cyanogen chloride in vapor form in the presence of an equivalent

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weight of an alkali metal hydroxide in a liquid hydrocarbon within the temperature range of substantially 0°–20° C.

7. A process for preparing a hydrocarbon substituted thiocyanate which comprises reacting the corresponding mercaptan with cyanogen chloride in vapor form in the presence of an equivalent weight of an alkali metal hydroxide in hexane.

8. A process for preparing a hydrocarbon substituted thiocyanate which comprises reacting the corresponding mercaptan with cyanogen chloride in vapor form in the presence of an equivalent weight of an alkali metal hydroxide in hexane within the temperature range of substantially 0°–50° C.

9. A process for preparing isopropyl thiocyanate which comprises reacting isopropyl mercaptan with cyanogen chloride in vapor form in the presence of an equivalent weight of an alkali metal hydroxide in benzene within the temperature range of substantially 0°–20° C.

10. A process for preparing tert-butyl thiocyanate which comprises reacting tert-butyl mercaptan with cyanogen chloride in vapor form in

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the presence of an equivalent weight of an alkali metal hydroxide in benzene within the temperature range of substantially 0°–20° C.

11. A process for preparing n-octyl thiocyanate which comprises reacting n-octyl mercaptan with cyanogen chloride in vapor form in the presence of an equivalent weight of an alkali metal hydroxide in hexane within the temperature range of substantially 0°–20° C.

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