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METHOD OF PRODUCING ALKYL THIOCYANATES AND SIMILAR ESTERS

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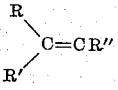
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7 Claims. (Cl. 260—98)

My invention relates to the production of alkyl thiocyanates and similar weak acid esters of the secondary and tertiary alcohols, and more particularly to the production of thiocyanates from the secondary and tertiary alkyl esters obtained from olefines and olefinic compounds.

One object of this invention is to provide a relatively simple process for the utilization of the olefines, higher than ethylene and other olefinic compounds to produce therefrom secondary and tertiary alkyl esters of relatively strong acids containing oxygen and to convert said esters into the secondary and tertiary alkyl esters of the weaker acids, for example, thiocyanic acid.

The object of this invention is to produce secondary alkyl thiocyanates from the secondary esters obtained from the reaction of a relatively strong acid containing oxygen, such as sulphuric acid, on the straight chain olefines of the type R·CH=CH·R′; on tertiary thiocyanates from the branched chain olefines of the type



in which olefines the carbon atom carrying a side chain also carries a double bond; and on secondary and tertiary thiocyanates from all other branched chain esters produced from olefines and olefinic compounds reacted with suitable acids containing oxygen, and to effect the production of the said thiocyanates without making it necessary to isolate the esters used for the purpose of producing the thiocyanates.

By olefinic compounds I mean those compounds which contain an ethylenic function and may contain other functions which may or may not inhibit or interfere with the normal reaction of the olefine with a relatively strong acid, such as sulphuric acid.

If, in these olefinic compounds there are present substituents or functions which tend to prevent the formation of the strong acid esters therefrom, or otherwise interfere with the reaction (as by producing or effecting a too rapid or a premature polymerization) they may be controlled in the usual ways, e. g., by acetylation or methylation, to render such interfering functions inactive or less active while the desired strong acid esters are being formed.

A further object of this invention is to react, a suitable, relatively strong acid, such as sulphuric acid with straight chain olefines of the type R·CH=CH·R′ and with branched chain olefines of the type



in which the carbon atom carrying a side chain, also carries a double bond, and with all other branched chain olefines and olefinic compounds and to produce, by such reaction secondary and tertiary alkyl esters of said strong acid and to thereafter convert the said secondary and tertiary esters into the secondary and tertiary esters of a relatively weaker acid such as thiocyanic acid in the presence of an excess of a relatively strong acid, which may be an excess of the strong acid employed to react with the olefines, and without making it necessary to isolate the esters formed from the agents employed or from the side products of the reactions.

Other objects of my invention will appear in the specification and claims below.

This invention relates to a method of making the secondary and tertiary alkyl esters of the weak acids, such as thiocyanic acid and consists essentially in effecting a cleavage in the secondary or tertiary alkyl esters of relatively strong acids, such as sulphuric acid, by a process somewhat similar to hydrolysis and which, for convenience, I term herein acidolysis.

I have discovered that with certain classes of alkyl esters, by process of acidolysis may be used to produce secondary and tertiary esters of thiocyanic acid. The extent to which the reaction is carried out and the nature of the products which are produced depend upon the conditions and the media in which the reaction takes place.

In primary alcohols, the radical carbon to oxygen bond is relatively strong and the oxygen to hydrogen bond is relatively weak. In tertiary alcohols, the radical carbon to oxygen bond is relatively weak and the oxygen to hydrogen bond is relatively strong, and in the secondary alcohols an intermediate position is present with respect to the nature of these bonds. This same relationship appears to hold with respect to the esters of these three types of alcohols and in the hydrolysis of these esters the point of cleavage is at the weaker bond or linkage.

Upon the treatment of the primary esters of the alcohols by any reagent analogous to water, such as a weak acid or an alcohol, a process analogous to hydrolysis occurs and yields, in part, the original alcohol and a derivation or product

of the acid originally employed for the production of the ester.

This may be exemplified by the reaction

$$RO\vdots OC\cdot CH_3+R'OH\rightleftharpoons R'OOC\cdot CH_3+ROH$$

wherein the point of cleavage is indicated by the dotted line.

Now if such a reaction is applied to the esters of the secondary alcohols or better to the esters of the tertiary alcohols, the following reaction takes place:

$$R\vdots OO\cdot CH_3+R'OH\rightarrow ROR'+CH_3COOH$$

due to the relative weakness of the carbon to oxygen bond.

It is this principle that I have discovered to apply to the treatment of secondary and tertiary esters by weak acids and it is the advantageous method of the application of this principle upon which this invention is based.

The general reaction may be, as above indicated, properly termed acidolysis and in its general form it may be expressed as follows:

$$R\vdots OOCR'+HX\rightarrow RX+R'COOH$$

in which R stands for any secondary or tertiary alkyl grouping and HX stands for a weak acid, such as thiocyanic acid, and the point of cleavage is at the dotted line.

Although in the exemplification above given I have shown, as the esters to be converted, the secondary and tertiary alkyl esters of monobasic carboxylic acids, which, by their simplicity, serve me here for illustrative purposes, I do not wish to be limited to the use of carboxylic acid esters, for I have found that the neutral or acid esters of strong polybasic acids, such as sulphuric or phosphoric acids, react to greater advantage in this relationship. These acids are outstandingly suitable, both on account of their high degrees of ionization in solution, and the stability of their acyl radicals, and are therefore herein termed "strong stable oxy-acids".

As a more specific example of my invention, I shall now refer to the reaction of thiocyanic acid upon a secondary or tertiary alkyl sulphuric ester, as follows:

$$R\vdots O\cdot SO_2\cdot OH+HSCN\rightarrow R\cdot SCN+H_2SO_4$$

in which R represents any secondary or tertiary alkyl grouping. Although in the above reaction the use of an acid ester of sulphuric acid is shown, I do not wish to exclude neutral esters, such as dialkyl sulphates which are of the type

$$R\cdot O\cdot SO_2\cdot O\cdot R$$

and which also react to advantage.

Although any method may be employed for the production of the secondary or tertiary alkyl esters for conversion into the esters of thiocyanic acid, I have found that a suitable ester or mixture of esters for the purpose is readily produced by subjecting the olefines, higher than ethylene, and olefinic compounds, to the action of a strong acid such as sulphuric acid or phosphoric acid of a proper concentration, or by reacting secondary or tertiary alcohols with sulphuric or other suitable acids containing oxygen and of proper concentrations.

For the preparation of secondary or tertiary esters of sulphuric acid from the various olefines, I attach a list of acid concentrations which may be used, but considerable variation is permissible in these acid concentrations, and I do not wish to be strictly limited by these examples.

For	Sulphuric acid
	Per cent concentration
2-methyl butene 2	62
Pentene 2	66
2-methyl propene 2	70
Butene 2	80
Propene	100

When phosphoric acid is used in the reaction with the olefines to produce the original secondary and tertiary esters, substantially stronger concentrations of the acid are required.

In performing my acidolysis reaction on original esters prepared by the reactions of strong stable oxy-acids with suitable olefines or with secondary or tertiary alcohols or, for that matter, prepared in any suitable manner, there should be present an excess of a strong stable oxy-acid, preferably, but not necessarily, the acid used in the production of the original esters.

As we ascend in the series of olefines, the tendency to polymerization increases under the influence of sulphuric acid. Accordingly, for use in my process, there must be selected an olefine which can be dissolved in a suitable strength of sulphuric acid with sufficient ease and rapidity that polymerization will not proceed extensively. There are certain olefines, generally those of more complex structure with which it is difficult to obtain a suitable reaction with sulphuric acid because polymerization will take place as rapidly as solution and reaction occur, and the presence of other functions in the olefine molecule may prevent the formation of stable sulphuric esters.

But by suitable precautions, such as adequate cooling, rapid agitation and protection of foreign substituents, as by acetylation or methylation, many olefines may be converted into suitable esters of strong stable oxy-acids. I wish, therefore, to have my invention construed as applying to whatever esters are preparable from acids and olefinic compounds, as discussed above.

In the practice of my invention involving the treatment of a secondary or tertiary alkyl ester with an acid like thiocyanic acid which is unstable in the free state, I find that the process may be advantageously practised by having with the ester or esters to be treated, an excess of free acid identical with or similar to that acid which was used in the preparation of the ester and in quantity sufficient to liberate from its salts enough thiocyanic acid to react completely with the ester present.

For instance, when the secondary or tertiary alkyl esters to be used have been prepared by the reaction of sulphuric acid with the olefines, more sulphuric acid is preferably used than is required to react to produce the required esters. The excess of the sulphuric acid will then be operative to liberate the thiocyanic acid which is added in the form of a salt, such as sodium thiocyanate.

In the case of readily volatile and more stable weak acids, such as hydrocyanic acid or hydrogen sulphide, the reaction may be carried on under pressure while the acids are added in gaseous form, and when so added and with the reaction taking place under normal pressure, means should be provided for collecting and dispensing

any excess gas that is not absorbed and reacted.

In the case of thiocyanic acid, which is not stable in the free state, I preferably add the sodium salt of thiocyanic acid in its solid form, to cooled and agitated mixtures of esters and free acid, taking care to add the salt sufficiently slowly that there is at no time any great concentration of free unreacted thiocyanic acid, which, under these conditions tends to polymerize to perthiocyanic acid and other products.

Example.—One molecular part of trimethylethylene (isoamylene) is reacted, by a suitable procedure with 2.5 molecular parts of 60% H_2SO_4, to produce a mixture containing tertiary amyl acid sulphate, di (tertiary amyl) sulphate and sulphuric acid. The mixture at a temperature of about 0° C., is vigorously agitated. Sodium thiocyanate (one molecular part) is now added in a slow stream, care being taken not to let the temperature rise more than a few degrees above zero. Agitation is allowed to continue for a few minutes after the addition is complete. An upper layer separates from the mixture and floats on the surface. This is removed, washed, neutralized with a mild alkali (10% Na_2CO_3 is suitable) and dried. The product is essentially tertiary amyl thiocyanate. It may be purified by distillation, collecting the distillate between 165°–170°, or by fractionation under vacuum, to produce a relatively pure product.

With higher olefines and with other olefinic compositions care should be taken to maintain the materials at a temperature which will prevent a too rapid polymerization of the composition and if necessary, any substituents of the olefinc compound may be rendered inactive to produce a rapid polymerization as by effecting an acetylation or methylation of the same during the production of the alkyl esters therefrom and during the conversion of said esters into the esters of the weaker acid.

A vigorous agitation with a consequent dispersion of the ester into minute suspended particles also accelerates the completion of the reaction so that the desired esters are producible notwithstanding the tendency toward polymerization which is constantly present. The time element is important, that is to say, care should be exercised to hasten the conversion of the heavy acid ester into the weaker acid ester and to retard as much as possible, and in the ways above indicated, the rate at which polymerization takes place during the process.

Having thus described my invention, what I claim and desire to protect by Letters Patent of the United States is:

1. The method of producing secondary and tertiary alkyl thiocyanates, which consists in agitating secondary and tertiary alkyl esters of acids stronger than thiocyanic and a salt of thiocyanic acid which is reacted upon by said stronger acid to release thiocyanic acid therefrom, whereby the liberated thiocyanic acid reacts with the alkyl residue of said stronger acid to produce therefrom secondary and tertiary alkyl thiocyanates.

2. The method of producing secondary and tertiary alkyl thiocyanates, which consists in agitating secondary and tertiary alkyl esters of sulphuric acid and a sodium salt of thiocyanic acid in the presence of a free acid which reacts with said salt to liberate thiocyanic acid therefrom, whereby the liberated thiocyanic acid reacts with the alkyl radical of the sulphuric acid esters to produce secondary and tertiary alkyl thiocyanates.

3. The method of producing secondary and tertiary alkyl thiocyanates, which consists in agitating secondary and tertiary alkyl esters of acids stronger than thiocyanic acid and hereinafter termed original esters, in the presence of a free acid stronger than thiocyanic acid and containing oxygen, and adding thereto, slowly during said agitation, a salt of thiocyanic acid which is reacted upon by said free stronger acid to liberate thiocyanic acid therefrom, whereby the liberated thiocyanic acid reacts with the alkyl radical of the original ester to produce secondary and tertiary alkyl thiocyanates and to produce from said original ester the strong acid which was a substituent of the said original ester.

4. The method of producing secondary and tertiary alkyl thiocyanates, which consists in agitating secondary and tertiary alkyl esters of strong stable oxy-acids and hereinafter termed original esters, in the presence of a free strong stable oxy-acid, and adding thereto, slowly during said agitation, a salt of thiocyanic acid which is reacted upon by said free acid to liberate thiocyanic acid therefrom, whereby the liberated thiocyanic acid reacts with the alkyl radical of the original ester to produce secondary and tertiary alkyl thiocyanates and to produce from said original ester the strong acid which was a substituent of the said original ester, a temperature not substantially higher than zero C. being maintained throughout the reaction.

5. The method of producing secondary and tertiary esters of thiocyanic acid and similar weak acids, which consists in agitating in a substantial excess of a strong acid containing oxygen, an olefine higher than ethylene and which does not polymerize rapidly in the presence of said strong acid under the conditions of the reaction to effect a conversion of the olefine into alkyl esters of the said acid, said esters being herein termed the original esters, and then cleaving the said original esters by acidolysis, which consists in agitating said original esters in the presence of thiocyanic acid at a temperature of substantially zero C., then allowing the resultant mixture to stratify and then separating the supernatant layer from the residue of said mixture.

6. The method of producing secondary and tertiary esters of thiocyanic acid, which consists in agitating an olefine with sulphuric acid in quantity in substantial excess of that required to effect the complete conversion of the olefine into the alkyl esters of said acid and herein termed the original esters and then cleaving said original esters so formed without isolating them or removing said excess acid by slowly adding to the mixture sodium thiocyanate and vigorously agitating the mixture, maintaining the temperature of the mixture at substantially zero C. whereby the thiocyanic acid released by the reaction reacts with the alkyl radical of the original ester to produce secondary and tertiary alkyl esters of thiocyanic acid, then allowing the mixture to stand and stratify and then separating the supernatant layer from the residue of the reaction.

7. The method of producing secondary and tertiary esters of thiocyanic acid, which consists in agitating an olefine with sulphuric acid in quantity in substantial excess of that required to effect the complete conversion of the olefine into the alkyl esters of said acid and herein termed the original esters and then cleaving said original esters so formed without isolating them or removing said excess acid by slowly adding

to the mixture sodium thiocyanate and vigorously agitating the mixture, maintaining the temperature of the mixture at substantially zero C. whereby the thiocyanic acid released by the reaction reacts with the alkyl radical of the original ester to produce secondary and tertiary alkyl esters of thiocyanic acid, then allowing the mixture to stand and stratify and then separating the supernatant layer from the residue of the reaction, and washing and drying the same and then purifying the said thiocyanates by distillation.

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