

# PATENT SPECIFICATION

Inventor: LESLIE SEED



795.824

Date of filing Complete Specification July 2, 1956.

Application Date Aug. 4, 1955.

No. 22443/55.

Complete Specification Published May 28, 1958.

Index at acceptance:—Class 2(3), C2B55XX.

International Classification:—C07c.

## COMPLETE SPECIFICATION

### Preparation of Esters of Hyponitrous Acid

5 We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement.

10 This invention relates to a new and improved method for the preparation of esters of hyponitrous acid. Esters of hyponitrous acid are according to known methods prepared by the reaction of an organic halide, preferably the iodide, with silver hyponitrite. They are  
15 unstable above 0° C. The inorganic salts of hyponitrous acid such as those of alkali metals can be prepared only in low yield, whilst silver hyponitrite must be prepared under very carefully controlled conditions, in the absence of  
20 light, and precipitated from very dilute solutions of reagents. Further, organic iodides as a class are not available in large quantity. For these reasons esters of hyponitrous acid have remained relatively rare, have not been manufactured on a commercial scale, and have not  
25 been much used in process chemistry, whilst their manufacture, if undertaken by known methods, would be uneconomic.

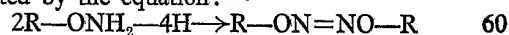
30 In recent years it has become known that esters of hyponitrous acid are valuable as initiators of free-radical type polymerisations. For example, British Specification No. 618,168 describes their use in the polymerisation of methyl methacrylate and vinyl chloride, but  
35 owing to the difficulty of preparing hyponitrous esters this valuable discovery has not been hitherto exploited.

40 It is an object of this invention to provide a new and improved process for preparing hyponitrous esters economically and in good yield.

45 According to our invention, esters of hyponitrous acid are prepared by the oxidation or dehydrogenation of O-ethers of hydroxylamine having the general formula  $R-O-NH_2$ , where

R is an organic radical, at temperatures below 50° C.

Compounds of this class, which may be described as O-ethers of hydroxylamine, may be prepared readily by the method of Traube, Ohlendorf and Zauder, as described in  
50 Berichte 53, 1477 (1920) or by some variant of the method which will be apparent to those skilled in the art. The O-ethers of hydroxylamine, when subjected to suitable oxidising or dehydrogenation conditions at temperatures below 50° C. and preferably below 0° C., yield  
55 esters of hyponitrous acid in a manner illustrated by the equation:—



The oxidation process may be carried out with the help of any convenient agent, for example mercuric oxide or another metallic compound in a higher valency state; halogens, their oxyacids and salts of the latter; peroxides  
65 both organic or inorganic; per-salts; oxygen, alone or in the presence of a carrier; azo compounds or other dehydrogenating agents; nitrous acid and its derivatives; other oxyacids, their anhydrides or salts. Particularly  
70 useful are the halogens and their oxy-salts formed when they react with alkaline or alkaline earth oxides or hydroxides.

The oxidation may be carried out electrolytically or the dehydrogenation may be carried out catalytically. It may be carried out under anhydrous or aqueous conditions; in alkaline, neutral or acid environments with undiluted reagents, or in the presence of an inert  
75 medium; in a homogeneous or in a heterogeneous system. A particularly useful method is in aqueous alkaline solution for then the hyponitrous esters separate from the reaction mixture as insoluble oils.

80 The products of the process of the invention when the lower alkoxyamines are used as starting materials possess all the characteristics of the corresponding hyponitrous esters prepared by known methods. They are sensitive to heat, friction and shock, and are prone  
90

to detonate with extreme violence; they are therefore difficult to characterise with precision, but their analyses and other properties are similar to the corresponding esters of hyponitrous acid prepared in the known manner. For example, their infra-red spectra are similar, particularly in having an absorption at  $1047\text{ cm}^{-1}$ , which we attribute to the C—O—N structure as it is present in hyponitrous esters—the corresponding band for the O-ethers of hydroxylamine is somewhat removed to below  $1040\text{ cm}^{-1}$ .

The invention is illustrated but not limited by the following example:—

#### EXAMPLE.

A solution of 22.5 gm. of caustic soda in 220 ml. of water is stirred at  $0^\circ\text{C}$ . whilst 45.7 gm. of bromine are added dropwise. The mixture is stirred at  $0^\circ\text{C}$ . for 30 minutes after the bromine has been taken into solution, and is then cooled to  $-10^\circ\text{C}$ . 10 gm. of ethoxylamine are then added drop by drop at sufficient intervals to permit the temperature to re-establish itself at  $-10^\circ\text{C}$ . After completion of the addition the mixture is stirred for 1 hour at  $-10^\circ\text{C}$ . and a yellow oil separates. The reaction mixture is extracted three times with 20 ml. of cold ether, the ether extract is washed three times with ice-water and is then dried over fused calcium chloride below  $0^\circ\text{C}$ . for 30 minutes. After removal of the calcium chloride by filtration, the ether is evaporated by rapidly drawing dry air through.

As residue is left a yellow oil which congeals to a viscous syrup at  $-80^\circ\text{C}$ . It con-

tains 23% of nitrogen ( $\text{C}_2\text{H}_6\text{O}_2\text{N}_2$  requires 23.7% N); it shows prominent infra-red bands at  $1047\text{ cm}^{-1}$ ,  $885\text{ cm}^{-1}$  and  $870\text{ cm}^{-1}$ , all of which are shown by ethyl hyponitrite when prepared in the known manner, and as the latter does it decomposes rapidly at room temperature with evolution of nitrogen.

What we claim is:—

1. A method for the preparation of an ester of hyponitrous acid that comprises oxidising or dehydrogenating an O-ether of hydroxylamine having the general formula  $\text{R—ONH}_2$ , in which R is an organic radical, at temperatures below  $50^\circ\text{C}$ .

2. A method for the preparation of an ester of hyponitrous acid as claimed in Claim 1 in which for oxidising the O-ether of hydroxylamine there is used an oxyacid salt of a halogen formed by reacting said halogen with a solution of an alkali hydroxide or alkaline earth hydroxide.

3. A method for the preparation of an ester of hyponitrous acid as claimed in Claim 2 in which the halogen is bromine and the hydroxide is sodium hydroxide.

4. A method for the preparation of an ester of hyponitrous acid as claimed in any of the preceding claims, in which the O-ether of hydroxylamine is ethoxylamine.

5. A method for the preparation of an ester of hyponitrous acid substantially as described in the foregoing example.

6. Esters of hyponitrous acid whenever prepared by the method of any of the foregoing claims.

ALFRED O. BALL,  
Agent for the Applicants.

### PROVISIONAL SPECIFICATION

#### Preparation of Esters of Hyponitrous Acid

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare this invention to be described in the following statement:—

This invention relates to a new and improved method for the preparation of esters of hyponitrous acid. Esters of hyponitrous acid are according to known methods prepared by the reaction of an organic halide, preferably the iodide, with silver hyponitrite. They are unstable above  $0^\circ\text{C}$ . The inorganic salts of hyponitrous acid such as those of alkali metals can be prepared only in low yield, whilst silver hyponitrite must be prepared under very carefully controlled conditions, in the absence of light, and precipitated from very dilute solutions of reagents. Further, organic iodides as a class are not available in large quantity. For these reasons esters of hyponitrous acid have remained relatively rare, have not been manufactured on a commercial scale, and have not been much used in process chemistry, whilst

their manufacture, if undertaken by known methods, would be uneconomic.

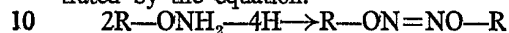
In recent years it has become known that esters of hyponitrous acid are valuable as initiators of free-radical type polymerisations. For example, Specification No. 618,168 describes their use in the polymerisation of methyl methacrylate and vinyl chloride, but owing to the difficulty of preparing hyponitrous esters this valuable discovery has not been hitherto exploited.

It is an object of this invention to provide a new and improved process for preparing hyponitrous esters economically and in good yield.

According to our invention, esters of hyponitrous acid are prepared by the oxidation or dehydrogenation of compounds having the general formula  $\text{R—ONH}_2$ , where R is an organic radical.

Compounds of this class, which may be described as O-ethers of hydroxylamine, may be prepared readily by the method of Traube,

Ohlendorf and Zauder, as described in *Berichte*, 53, 1477 (1920) or by some variant of the method which will be apparent to those skilled in the art. The O-ethers of hydroxylamine, when subjected to suitable oxidising or dehydrogenation conditions at temperatures below 50° C. and preferably below 0° C. yield esters of hyponitrous acid in a manner illustrated by the equation.



The oxidation process may be carried out with the help of any convenient agent, for example mercuric oxide or another metallic compound in a higher valency state; halogens, their oxy-acids and salts of the latter; peroxides both organic or inorganic; per-salts; oxygen, alone or in the presence of a carrier; azo compounds or other dehydrogenating agents; nitrous acid and its derivatives; other oxyacids, their anhydrides or salts. Particularly useful are the halogens and their oxy-salts formed when they react with alkaline or alkaline earth oxides or hydroxides.

The oxidation may be carried out electrolytically or the dehydrogenation may be carried out catalytically. It may be carried out under anhydrous or aqueous conditions; in alkaline, neutral or acid environments with undiluted reagents, or in the presence of an inert medium; in a homogeneous or in a hetero-phase system. A particularly useful method is in aqueous alkaline solution for then the hyponitrous esters separate from the reaction mixture as insoluble oils.

The products of the process of the invention when the lower alkoxyamines are used as starting materials possess all the characteristics of the corresponding hyponitrous esters prepared by known methods. They are sensitive to heat, friction and shock, and are prone to detonate with extreme violence; they are therefore difficult to characterise with precision, but their

analyses and other properties are similar to the corresponding esters of hyponitrous acid prepared in the known manner. For example, their infra-red spectra are similar, particularly in having an absorption at 1047 cm<sup>-1</sup>, which we attribute to the C—O—N structure as it is present in hyponitrous esters—the corresponding band for the O-ethers of hydroxylamine is somewhat removed to below 1040 cm<sup>-1</sup>.

The invention is illustrated but not limited by the following example.

#### EXAMPLE.

A solution of 22.5 gm. of caustic soda in 220 ml. of water is stirred at 0° C. whilst 45.7 gm. of bromine are added dropwise. The mixture is stirred at 0° C. for 30 minutes after the bromine has been taken into solution, and is then cooled to -10° C. 10 gm. of ethoxylamine are then added drop by drop at sufficient intervals to permit the temperature to re-establish itself at -10° C. After completion of the addition the mixture is stirred for 1 hour at -10° C. and a yellow oil separates. The reaction mixture is extracted three times with 20 ml. of cold ether, the ether extract is washed three times with ice-water and is then dried over fused calcium chloride below 0° C. for 30 minutes. After removal of the calcium chloride by filtration, the ether is evaporated by rapidly drawing dry air through.

As residue is left a yellow oil which congeals to a viscous syrup at -80° C. It contains 23% of nitrogen (C<sub>4</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub> requires 23.7% N); it shows prominent infra-red bands at 1047 cm<sup>-1</sup>, 885 cm<sup>-1</sup> and 870 cm<sup>-1</sup>, all of which are shown by ethyl hyponitrite when prepared in the known manner, and as the latter does it decomposes rapidly at room temperature with evolution of nitrogen.

ALFRED O. BALL,

Agent for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press,—1958.

Published at the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.