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PRODUCTION OF TRICHLOROBENZOIC ACID

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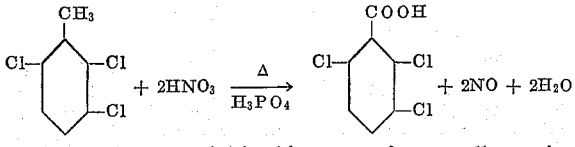
This invention relates to the production of trichlorobenzoic acid. More specifically it relates to the production of 2,3,6-trichlorobenzoic acid and to the production of mixtures of trichlorobenzoic acid isomers including substantial amounts of the 2,3,6-isomer.

Trichlorotoluenes, and particularly those trichlorotoluenes having chlorine atoms in the two ring positions adjacent to the methyl group, are relatively non-reactive compounds. It is difficult to oxidize these compounds to the corresponding chlorinated benzoic acids. It is especially difficult to oxidize them to the corresponding acids without introducing undesirable substituents into the ring or into the side chain.

Attempts to prepare 2,3,6-trichlorobenzoic acid by procedures involving the direct oxidation of 2,3,6-trichlorotoluene have heretofore been unsuccessful in that they give low yields of the acid and are often difficult and costly to operate. For example, treatment of trichlorotoluene containing approximately 65% of the 2,3,6-isomer with 70% nitric acid at reflux temperature for 12 hours resulted in a 2.5% yield of acid products. The use of more concentrated nitric acid resulted in nitrated products. Brimelow et al. (J.C.S., 1951, 1208–12) heated 2,3,6-trichlorotoluene with a large excess of 60% nitric acid under superatmospheric pressure at 150° C. for 6 hours and obtained a low yield of 2,3,6-trichlorobenzoic acid. The Brimelow et al. process is commercially impractical because it requires the use of specially constructed pressure equipment and because it yields relatively small amounts of the desired product. Procedures used commercially for the production of 2,3,6-trichlorobenzoic acid usually involve the chlorination of 2,3,6-trichlorotoluene to form 2,3,6-trichlorobenzal chloride, conversion of this compound to 2,3,6-trichlorobenzaldehyde, and oxidation of the aldehyde to the desired acid.

It has been found that trichlorotoluene may be oxidized directly to trichlorobenzoic acid by heating it under substantially atmospheric pressure with concentrated nitric acid in the presence of phosphoric acid. This oxidation, which may be carried out in ordinary processing equipment, results in a relatively high yield of trichlorobenzoic acid of approximately the same 2,3,6-isomer content as the starting material. The products obtained by this procedure contain only very small amounts of nitrated reaction by-products.

In accordance with this invention trichlorotoluene containing 2,3,6-trichlorotoluene is brought into contact with concentrated nitric acid and concentrated phosphoric acid at an elevated temperature and under substantially atmospheric pressure to form the desired acid. The primary reaction proceeds as follows:



The starting material in this process is generally a mixture of trichlorotoluenes containing a substantial amount of the 2,3,6-isomer. This material may be prepared, for example, by chlorinating toluene, o-chlorotoluene, an appropriate dichlorotoluene, or mixtures of these compounds in the presence of a nuclear-chlorinating catalyst, such as aluminum chloride or iron filings. Alternatively, pure or

substantially pure 2,3,6-trichlorotoluene may be used as the starting material.

The trichlorotoluene is oxidized with concentrated nitric acid containing at least 85% HNO_3. Preferably 90%–100% acid is used. The percentage figure used refers to the HNO_3 content of the acid, the remainder being water plus the small amount of impurities which may be present in commercial grades of nitric acid. For example, 90% nitric acid refers to acid containing by weight 90% of HNO_3 and 10% of water and impurities. Concentrated nitric acid containing dissolved nitrogen oxides may also be used in this procedure.

As indicated by the above equation, nitrogen monoxide (NO) is a by-product of the nitric acid oxidation of trichlorotoluene. This material may be collected and oxidized with air or oxygen to nitrogen dioxide, NO_2, which may be used in combination with concentrated nitric acid in subsequent oxidations. Alternatively, concentrated nitric acid containing as much as 15% of nitrogen dioxide may be used as the oxidizing agent. When the oxidation is carried out in accordance with the present invention, only very small amounts of nitrated by-products are present in the product.

The amount of nitric acid used in the oxidation is at least that required stoichiometrically. An excess of acid is usually employed to insure a maximum conversion of trichlorotoluene to trichlorobenzoic acid. This excess may range from approximately 5% to 100%. Excellent yields are obtained when an excess of approximately 10% to 25% is used. Inasmuch as two moles of nitric acid is required to oxidize one mole of trichlorotoluene (see above equation), the amount of nitric acid used in the oxidation is in the range of approximately 2 to 4 moles for each mole of trichlorotoluene. Preferably 2.1 to 2.5 moles is used for each mole of trichlorotoluene.

The oxidation of trichlorotoluene to trichlorobenzoic acid in accordance with this invention is effected under substantially atmospheric pressure at a temperature between approximately 150° and 230° C., preferably between 160° and 180° C. At temperatures below this range the oxidation takes place slowly and gives poor yields of trichlorobenzoic acid; at higher temperatures decomposition of the product may occur.

Nitric acid forms with water an azeotrope that contains 68% of nitric acid and that boils at 120.5° C. Since water is added to the trichlorotoluene-nitric acid reaction mixture along with the nitric acid and is formed as a reaction product, it is ordinarily not possible to carry out the oxidation of trichlorotoluene in the temperature range required for efficient operation without the use of superatmospheric pressure.

I have found that the addition of phosphoric acid to the trichlorotoluene-nitric acid-water system allows the nitric acid and water to exist in a stable system at atmospheric pressure at the elevated temperatures required for a suitable reaction rate. Unlike sulfuric acid in similar systems, phosphoric acid has little tendency to form with the water present hydrates that favor the formation of those nitrogen oxides, e.g. nitrogen pentoxide (N_2O_5), that act as nitrating agents.

As used herein the term "phosphoric acid" includes all forms of this acid, for example, pyrophosphoric acid, polyphosphoric acid, hypophosphoric acid, metaphosphoric acid, and orthophosphoric acid. Acid of at least 90% concentration is preferred in the reaction, since the use of less concentrated acid results in a reaction mixture having a boiling point lower than the desired reaction temperature. To obtain a reaction temperature between 150° and 230° C. it is necessary that there be present in the reaction mixture approximately 0.8 to 3.0 moles of phosphoric acid for each mole of nitric acid. Optimum re-

sults are obtained when approximately 1 to 2 moles of phosphoric acid is used for each mole of nitric acid.

The phosphoric acid may be mixed with the trichlorotoluene before the addition of nitric acid is begun, or a mixture of phosphoric acid and nitric acid may be added to the trichlorotoluene. Alternatively, a mixture of nitric acid and a portion of the phosphoric acid may be added to a mixture of trichlorotoluene and the remainder of the phosphoric acid.

When nitric acid or phosphoric acid of less than 100% concentration is used in the oxidation of trichlorotoluene, water is introduced into the reaction mixture. In addition two moles of water is formed during the reaction for each mole of trichlorobenzoic acid. As has been indicated, the presence of water results in a lowering of the boiling point of the reaction mixture and thus in a lowering of the maximum temperature that can be attained under substantially atmospheric pressure. I have found that if the initial amount of water added with the nitric acid and the phosphoric acid is in the range of approximately 0.15 to 0.45 mole per mole of phosphoric acid, the reaction temperature remains in the desired range throughout the oxidation. While the formation of water during the reaction lowers the boiling point of the reaction mixture, the temperature remains in the desired range when the specified amount of water is added initially with the nitric acid and phosphoric acid.

The oxidation is preferably carried out by heating a mixture of trichlorotoluene and phosphoric acid to 170°–180° C. and slowly adding to it a mixture of nitric acid and phosphoric acid. As the reaction takes place, water is formed, and the boiling point of the mixture is gradually lowered. When its boiling point has fallen to 170°–180° C., the reaction mixture will begin to reflux. Continuation of the oxidation will cause the boiling point to fall further. When the specified amounts of phosphoric acid, water, and nitric acid are employed, the boiling point at the end of the reaction is approximately 160°–165° C.

The time required for the oxidation is dependent to a large extent upon the reaction temperature and upon the rate at which nitric acid is introduced into the reaction vessel. At temperatures in the lower portion of the specified range, the oxidation takes place relatively slowly. Less time is required at higher temperatures. The nitric acid is added to the trichlorotoluene reaction mixture at approximately the same rate as it is consumed in the oxidation. This rate of addition prevents the accumulation in the reaction vessel of a large excess of nitric acid, which might cause product decomposition. The slow addition also prevents an undue loss of by-product nitrogen dioxide from the reaction mixture, thereby increasing the oxidizing capacity of the acid. In most cases the oxidation is substantially complete just after the last of the nitric acid has been added.

Although no catalyst is required for the oxidation, I have found that improved yields of the product are obtained when the reaction is carried out in strong visible light.

The trichlorobenzoic acid prepared in accordance with the present invention may be separated from the reaction mixture by any suitable procedure. For example, the mixture may be washed with water to separate the inorganic acids from the trichlorobenzoic acid. The product obtained is a mixture of trichlorobenzoic acid isomers having approximately the same 2,3,6-isomer content as the starting material. The 2,3,6-isomer content of the product may be increased, or the 2,3,6-isomer may be separated from the other isomers by various procedures. One suitable procedure, which is described in the copending application of George M. Sieger, Serial No. 546,811, filed November 14, 1955, involves the fractional crystallization of a mixture of isomers of trichlorobenzoic acid

The invention is illustrated by the examples that follow. It should be understood, however, that the examples are given by way of illustration only and that the invention is not to be limited by the details set forth therein.

Example 1

To a mixture of 200 grams (1.02 moles) of trichlorotoluene containing approximately 65% of 2,3,6-trichlorotoluene and 200 grams of 100% phosphoric acid at a temperature of 170°–180° C. was added dropwise over a period of 20 hours an acid mixture made up of 164 grams (2.35 moles) of 90% nitric acid and 164 grams (1.67 moles) of 100% phosphoric acid. The oxidation was carried out in the presence of light from a mercury arc lamp. During the final stages of the addition the reaction mixture began to reflux. At the end of the addition, the temperature of the refluxing reaction mixture had fallen to 160° C.

The oxidized reaction mixture was diluted with 300 ml. of water. The layers that formed were separated; the aqueous layer was discarded, and the organic layer was washed with 200 grams of hot water. A mixture of the organic layer and 500 grams of water was brought to pH 7–8 with alkali and was then filtered. Following clarification with charcoal and filter-aid, the aqueous extract was acidified with concentrated hydrochloric acid. The material that precipitated was collected, washed with two 100 gram portions of cold water, and dried in a vacuum oven at 55°–60° C. There was obtained by this procedure a 78% yield (180 grams) of a mixture of trichlorobenzoic acids that contained approximately 60% of 2,3,6-trichlorobenzoic acid.

Example 2

To a mixture of 200 grams (1.02 moles) of trichlorotoluene containing approximately 65% of 2,3,6-trichlorotoluene and 200 grams (2.0 moles) of 100% phosphoric acid which had been heated to 170°–180° C. was added dropwise in the absence of light an acid mixture made up of 164 grams (2.35 moles) of 90% nitric acid and 164 grams (1.67 moles) of 100% phosphoric acid. Approximately 20 hours was required for the addition.

The oxidized reaction mixture was worked up by the procedure described in Example 1. There was obtained a 71.6% yield of a trichlorobenzoic acid mixture that contained approximately 60% of the 2,3,6-isomer.

2,3,6-trichlorobenzoic acid and mixtures of trichlorobenzoic acids containing substantial amounts of the 2,3,6-isomer find wide-spread use as herbicides, especially as selective herbicides for the elimination of broad-leafed weeds from fields of corn or sugarcane. The present invention has, therefore, been described as a method for the conversion of trichlorotoluene containing 2,3,6-trichlorotoluene to trichlorobenzoic acid containing 2,3,6-trichlorobenzoic acid. It should be understood, however, that this procedure may be used to convert other substituted toluenes to substituted benzoic acids. For example, the other isomers of trichlorotoluene, that is to say, the 2,3,4-isomer, the 2,3,5-isomer, the 2,4,6-isomer, the 2,4,5-isomer, and the 3,4,5-isomer, may be converted to the corresponding isomers of trichlorobenzoic acid by the procedure of this invention. This procedure is of particular value in converting to the corresponding polychlorobenzoic acids polychlorotoluenes having chlorine in at least the two ring positions adjacent to the methyl group. Thus, 2,6-dichlorotoluene may be oxidized to 2,6-dichlorobenzoic acid; 2,3,5,6-tetrachlorotoluene to 2,3,5,6-tetrachlorobenzoic acid; and 2,3,4,5,6-pentachlorotoluene to 2,3,4,5,6-pentachlorobenzoic acid. Similarly mixtures of polychlorobenzoic acids having chlorine atoms in at least the 2 and 6 positions may be prepared by this procedure.

This procedure may also be applied to other aromatic or polycyclic hydrocarbons which contain at least one alkyl group and one or more non-oxidizable groups as substituents. These include, for example, toluenes, xylenes, and methylnaphthalenes having as substituents

such non-oxidizable groups as —NO_2, —F, —Br, —CF_3, and the like.

I claim:

1. A process for the production of polychlorobenzoic acid comprising oxidizing polychlorotoluene at a temperature between approximately 150° C. and approximately 230° C. and under substantially atmospheric pressure with at least the stoichiometric amount of concentrated nitric acid in the presence of concentrated phosphoric acid in the amount of approximately 0.8 mole to 3.0 moles of said phosphoric acid per mole of said nitric acid.

2. A process for the production of polychlorobenzoic acid comprising heating polychlorotoluene at a temperature between approximately 150° C. and approximately 230° C. and under substantially atmospheric pressure with at least the stoichiometric amount of nitric acid of at least 85% HNO_3 concentration and phosphoric acid of at least 90% concentration in the amount of approximately 0.8 mole to 3.0 moles of said phosphoric acid per mole of said nitric acid.

3. A process for the production of a mixture of trichlorobenzoic acid isomers including 2,3,6-trichlorobenzoic acid comprising heating a mixture of trichlorotoluene isomers including 2,3,6-trichlorotoluene at a temperature between approximately 150° C. and approximately 230° C. and under substantially atmospheric pressure with at least the stoichiometric amount of concentrated nitric acid in the presence of concentrated phosphoric acid in the amount of approximately 0.8 mole to 3.0 moles of said phosphoric acid per mole of said nitric acid, thereby producing a mixture of trichlorobenzoic acid isomers including the 2,3,6-isomer.

4. A process for the production of a mixture of trichlorobenzoic acid isomers including the 2,3,6-isomer comprising heating a mixture of trichlorotoluene isomers including the 2,3,6-isomer at a temperature between approximately 150° C. and approximately 230° C. and under substantially atmospheric pressure with nitric acid and phosphoric acid, said nitric acid having a HNO_3 content of at least 85% and being present in the amount of approximately 2 to 4 moles for each mole of trichlorotoluene, and said phosphoric acid being of at least 90% concentration and present in the amount of approximately 0.8 to 3 moles for each mole of nitric acid, to produce a mixture of trichlorobenzoic acid isomers including the 2,3,6-isomer.

5. A process for the production of a mixture of trichlorobenzoic acid isomers including the 2,3,6-isomer comprising heating a mixture of trichlorotoluene isomers including the 2,3,6-isomer at a temperature of approximately 160°–180° C. and under substantially atmospheric pressure with nitric acid and phosphoric acid in the presence of strong visible light, said nitric acid having a HNO_3 content of at least 90% and being present in the amount of approximately 2.1 to 2.5 moles for each mole of trichlorotoluene, and said phosphoric acid being of at least 90% concentration and present in the amount of approximately 1 to 2 moles for each mole of nitric acid to produce a mixture of trichlorobenzoic acid isomers including the 2,3,6-isomer.

6. A process for the production of a mixture of trichlorobenzoic acid isomers including the 2,3,6-isomer comprising heating a mixture of isomers of trichlorotoluene including the 2,3,6-isomer at a temperature of approximately 150°–230° C. and under substantially atmospheric pressure with nitric acid, phosphoric acid and an initial amount of water, said nitric acid being present in the amount of approximately 2 to 4 moles for each mole of trichlorotoluene, and said phosphoric acid being present in the amount of approximately 0.8 to 3 moles for each mole of nitric acid, the initial amount of water present being approximately 0.15 to 0.45 mole for each mole of phosphoric acid, to produce a mixture of trichlorobenzoic acid isomers including the 2,3,6-isomer.

7. A process for the production of a mixture of trichlorobenzoic acid isomers including the 2,3,6-isomer comprising heating a mixture of trichlorotoluene isomers including the 2,3,6-isomer at a temperature of approximately 160°–180° C. and under substantially atmospheric pressure with nitric acid and phosphoric acid in the presence of strong visible light, said nitric acid being present in the amount of approximately 2.1 to 2.5 moles for each mole of trichlorotoluene and comprising a mixture of water and at least 90% HNO_3, and said phosphoric acid being present in the amount of approximately 1 to 2 moles for each mole of nitric acid and comprising a mixture of water and at least 90% phosphoric acid, the total amount of water added in said nitric acid and said phosphoric acid being approximately 0.15 to 0.45 mole for each mole of phosphoric acid, to produce a mixture of trichlorobenzoic acid isomers including the 2,3,6-isomer.

8. A process for the production of 2,3,6-trichlorobenzoic acid comprising the steps of heating a mixture of trichlorotoluene isomers including the 2,3,6-isomer at a temperature of approximately 150°–230° C. and under substantially atmospheric pressure with nitric acid and phosphoric acid, said nitric acid having a HNO_3 content of at least 85% and being present in the amount of approximately 2 to 4 moles for each mole of trichlorotoluene and said phosphoric acid being of at least 90% concentration and present in the amount of approximately 0.8 to 3 moles for each mole of nitric acid, to produce a mixture of trichlorobenzoic acid isomers including the 2,3,6-isomer, and thereafter separating said 2,3,6-trichlorobenzoic acid from said mixture of trichlorobenzoic acid isomers.

9. A process for the production of 2,3,6-trichlorobenzoic acid comprising heating 2,3,6-trichlorotoluene at a temperature between approximately 150° and 230° C. and at substantially atmospheric pressure with nitric acid and phosphoric acid, said nitric acid having a HNO_3 content of at least 85% and being present in the amount of approximately 2 to 4 moles for each mole of 2,3,6-trichlorotoluene, and said phosphoric acid being of at least 90% concentration and present in the amount of approximately 0.8 to 3 moles for each mole of nitric acid, to produce 2,3,6-trichlorobenzoic acid.

10. A process for the production of trichlorobenzoic acid comprising heating trichlorotoluene at a temperature between approximately 150° C. and approximately 230° C. and under substantially atmospheric pressure with at least the stoichiometric amount of concentrated nitric acid in the presence of concentrated phosphoric acid in the amount of approximately 0.8 mole to 3.0 moles of said phosphoric acid per hole of said nitric acid, thereby producing trichlorobenzoic acid.

References Cited in the file of this patent

Brimelow et al.: Chem. Absts., vol. 46, columns 2002–3 (1952).