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PROCESS FOR THE PRODUCTION OF 1-NITRO-ANTHRAQUINONE-6-CARBOXYLIC ACID AND CARBONYL HALIDES THEREOF

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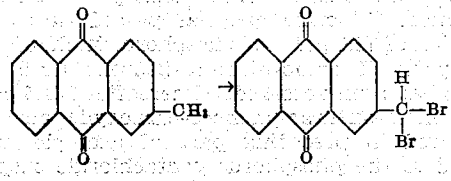
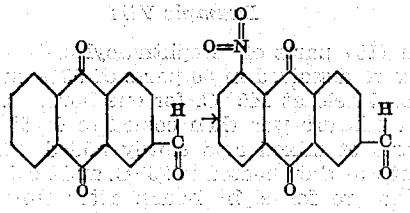
5 Claims. (Cl. 260—57)

This invention relates to the preparation of carbon compounds and more particularly to the preparation of 1-nitro-anthraquinone-6-carboxylic acid and its corresponding carbonyl halides.

The compound 1-nitro-anthraquinone-6-carboxylic acid has heretofore been produced but by a most complicated procedure. In 1914 Eckert (Monats. 35, 289–296) treated 2-methyl-anthraquinone to produce omega-di-bromo-2-methyl-anthraquinone. The conversion is indicated by the following equation.



He thereafter hydrolyzed the di-bromo compound to produce the corresponding anthraquinone-2-aldehyde and nitrated this product to produce 1-nitro-anthraquinone-6-aldehyde according to the equation:



Subsequent oxidation converted the aldehyde to the corresponding (1-nitro-anthraquinone-6-carboxylic acid) acid.

This invention has for an object the preparation of 1-nitro-anthraquinone-6-carboxylic acid and its corresponding carbonyl halides by improved processes. Other objects are the preparation of these compounds in a very desirable physical form and their preparation in a high state of purity. Still further objects are the preparation of new chemical compounds and new chemical processes. A general advance in the art and other objects which will appear hereinafter was contemplated.

In general, the invention comprises treating terephthaloyl-ortho-benzoic acid with sulphuric acid followed by a treatment with a nitrating substance and finally treating the resultant product with a substance capable of converting a carboxyl group to a carbonyl halide.

The invention will be further understood from a consideration of the following detailed description and specific examples in which the parts are given by weight.

Example I

Ten (10) parts of terephthaloyl-ortho-benzoic acid were dissolved in 100 parts of sulphuric acid (100%) and held at a temperature of 150° C. for 2–3 hours, after which the solution was cooled to 5–10° C. Twelve (12) to 14 parts of a mixture comprising 32% nitric acid (HNO_3) and 68% sulphuric acid (H_2SO_4), hereinafter referred to as mixed acid, were then added to the solution. The temperature of the solution was allowed to rise to 35° C. and held there for one hour after which it was drowned in water and filtered. The filter cake was dried and extracted with 10 parts of hot glacial acetic acid. The insoluble part remaining was substantially pure 1-nitro-anthraquinone-6-carboxylic acid. One part of this product was heated with one part phosphorus pentachloride and 6–8 parts of solvent naphtha. The resultant 1-nitro-anthraquinone-6-carbonyl chloride was filtered cold, washed with benzene and dried. The 1-nitro-anthraquinone-6-carboxylic acid is a grey to grey yellow colored product dissolving in concentrated sulphuric acid producing a yellow solution and in dilute alkali producing a red solution. The 1-nitro-anthraquinone-6-carbonyl chloride is a light yellow colored product characterized by the reactions common to nitro substituents, vatting carbonyl groups and carbonyl chloride radicals. This product as above produced has a sharp melting point near 196° C. It gives a yellow solution color in concentrated sulphuric acid.

Example II

Ten (10) parts of terephthaloyl-ortho-benzoic acid were dissolved in 80 parts of sulphuric acid (100%) and held at a temperature of 150° C. for one hour after which the solution was cooled to 10–20° C. and 8 parts of mixed acid slowly added. After three hours agitation at the same temperature the mixture was drowned in water and filtered. The filter cake was then dissolved in dilute alkali by warming (in this instance sodium hydroxide) and allowed to cool. Thereafter the alkali metal salt of the 1-nitro-anthraquinone-6-carboxylic acid which separated out, was filtered off. From this alkali metal salt the 1-nitro-anthraquinone-6-carboxylic acid was obtained by dissolving the alkali metal salt in water in the ratio of about 275 parts of the alkali metal salt to 5000–8000 parts of water. Thereafter the water solution was acidified with sulphuric acid

(other acids, for example hydrochloric, may be used) to the point where the medium was acid to Congo red and heated at the boiling point for one hour. The solid 1-nitro-anthraquinone-6-carboxylic acid was then filtered off. From the dried 1-nitro-anthraquinone-6-carboxylic acid the corresponding carbonyl chloride was obtained by heating one part of the same in four parts of ortho-dichloro-benzene with one part of phosphorus pentachloride until the conversion was complete as indicated by solution of the acid chloride.

Example III

Ten (10) parts of terephthaloyl-ortho-benzoic acid were dissolved in 100 parts of concentrated sulphuric acid (96–98%) and heated at 135°–140° C. for three hours. After cooling the resultant mass to 0° C.–5° C. 6–7 parts of nitric acid (Sp. Gr. 1.42) were slowly added. The temperature was allowed to rise to 30–40° C. and held at this point for 2–4 hours after which time the mixture was drowned in water and filtered. The residue was then dissolved in dilute sodium hydroxide and a sufficient amount of sodium chloride added to produce an 8% sodium chloride solution. The sodium salt of the 1-nitro-anthraquinone-6-carboxylic acid, which separated out was filtered and washed with 10% sodium chloride solution. The free acid was prepared from the alkali metal salt by suspending the same into about 50 parts of water and heating to 85–90° C. at which temperature sufficient hydrochloric acid was added to make this suspension distinctly acidic in character. The mass was held at about 90° C. from 2–4 hours filtered and the cake washed acid free and dried. The dried, free acid was converted to 1-nitro-anthraquinone-6-carbonyl bromide by treatment with phosphorus pentabromide in a manner similar to that set out in Example I.

Example IV

One (1) part of the alkali metal salt of 1-nitro-anthraquinone-6-carboxylic acid and one part of phosphorus pentachloride were added to 7 parts of ortho-di-chloro-benzene. The whole was then slowly heated to 90° C.–100° C. and held at that temperature for one-half hour after which it was filtered at 95° C. (in order to remove the alkali metal chloride present) and the filtrate cooled to 10° C.–15° C. Thereafter the 1-nitro-anthraquinone-6-carbonyl chloride was filtered off and washed first with one part of ortho-di-chloro-benzene and second with 2–3 parts of benzene. The cake was then dried.

Example V

Ten (10) parts of terephthaloyl-ortho-benzoic acid were dissolved in 80 parts of sulphuric acid (100%) and held at a temperature of 150° C. for one hour. The solution was then cooled to 0°–5° C. Ten (10) parts of mixed acid were then slowly added and after one half hour at 5° C. the solution temperature raised to 20–25° C. The temperature was maintained at this point for 8–10 hours after which the mass was drowned in cold water, and filtered. The residue after drying, was added to 12–15 times its weight of boiling glacial acetic acid. After boiling the resultant for one half to one hour, it was cooled to about 90–100° C. and filtered.

Example VI

Ten (10) parts of terephthaloyl-ortho-benzoic acid were dissolved in 88 parts of sulphuric acid (100%) and held at a temperature of 150° C. for about two hours, after which the solution was cooled to 10–20° C. and sufficient water added to produce a sulphuric acid concentration of 95%. Thereafter dry sodium nitrite (14–18 parts) was added in small portions over 4–5 hours while maintaining the temperature at 20° C. The mass was then allowed to stand at 20–25° C. for 8–10 hours after which it was drowned in cold water. From this reaction product the 1-nitro-anthraquinone-6-carboxylic acid can be isolated and converted to the corresponding carbonyl halide in the manner described in the other examples.

Example VII

One hundred eighty-five (185) parts of terephthaloyl-ortho-benzoic acid were dissolved in 1660 parts of 97% sulphuric acid and held at a temperature of 140° C. for ¾ hr. The solution was then cooled to 0°–5° C. Thereafter 222 parts of mixed acid were slowly added. When the addition was finished the temperature was allowed to rise to 25–30° C. After holding the reaction mass at this temperature for 6–8 hours, water was slowly added, a quantity sufficient to reduce the sulphuric acid concentration to 88%. The charge was then agitated for one hour at 25° C. and filtered. The residue was first washed with 85% sulphuric acid and then washed with water until acid free. The residue was then dried and it was found that a yield of 131.5 parts had been obtained. Chlorine gas was passed through a solution of 73.6 parts of phosphorus trichloride in 525 parts of ortho-dichloro-benzene until 38.1 parts had been absorbed. Thereafter 131.5 parts of 1-nitro-anthraquinone-6-carboxylic acid, as prepared in preceding part of example, were added to the phosphorus pentachloride suspension in ortho-dichloro-benzene. The resultant was heated 90–100° C. until complete solution had taken place which mass was then cooled and filtered at 20° C. The residue was washed with benzene and dried.

Example VIII

Ten (10) parts of terephthaloyl-ortho-benzoic acid were dissolved in 90 parts of 95% sulphuric acid and held at 140° C. for one hour. This reaction mixture was then cooled to 0°–5° C. and 12 parts of mixed acid slowly added. The resultant was then heated to 25° C. and held at that temperature for eight hours, after which time sufficient water was added to reduce the sulphuric acid concentrations to 83%. The charge was then agitated for one-half hour at 25° C., filtered, washed with 80% sulphuric acid and washed with water until acid free. The filter cake was then dissolved in dilute alkali and salted out from an 8% solution of sodium chloride in the manner previously described. The solid material was filtered and converted to the free 1-nitro-anthraquinone-6-carboxylic acid in the manner previously set out. This product was dried and added to ten times its weight of thionyl chloride. The suspension was refluxed from 1–2 hours and excess thionyl chloride was distilled off. While this product is in very desirable physical form and of high purity, if desired it may be further treated by slurring in six times its weight of benzene. The benzene may be removed by filtration.

It will be appreciated that the above examples are given merely for the purpose of illustrating the invention. Wide variations from the exact

procedure set out in these examples will suggest themselves to those skilled in the art.

As illustrative of the wide variations which fall within the scope of the invention the following may be mentioned. In the first step in the process the best results have been obtained with 96–100% sulphuric acid. Sulphuric acid concentrations from 10% oleum (102.3% H_2SO_4) down to 95% have been advantageously employed. In this range the lower concentrations range of 100%–95% is preferred. Good results are obtainable with concentrations extending below the above range, for example 95%–90% and lower. The following table gives several specific sets of conditions for the first step in the process which produces excellent results.

Table I

H_2SO_4 parts by weight	H_2SO_4 Concentration	Reaction temperature	Time of reaction in hours
8–10	10% Oleum	100°–130° C.	1–3
8–10	100%	140°–150° C.	½–1
8–10	100%	150° C.	½
8–10	100%	160°–165° C.	½–1
6	100%	160° C.	1–2
10	97-98%	150° C.–160° C.	1 hr.–2 hr.
9	96%	145–150° C.	1–1½
10	94–96%	160°–170° C.	2–3
20	93%	165°–190° C.	2–4

In each of the above specific sets of conditions one part of the starting material (terephthaloyl-ortho-benzoic acid) is used. All things considered, the preferred conditions involve one part of terephthaloyl-ortho-benzoic acid, 8 parts of 98% H_2SO_4 and a reaction temperature of 140–150° C. for one half to one hour.

For the second step in the process an amount of nitric acid somewhat in excess of that required to molecularly combine with the product being treated is used in order that 1-nitro group may be introduced into the nucleus. It is possible to prepare a good quality of product in good yield in the absence of an excess of nitric acid so it is therefore to be understood that the excess is not critical. The excess nitric acid does not appear to deleteriously affect the reaction since as much as 100% excess nitric acid has been used without detriment to the process or product.

In the second step in which nitric acid is added to the reaction mass it is preferred that the concentration of the sulphuric acid be 92–96%, more particularly 94%. This percentage range is not critical since the process operates satisfactorily with the use of 100% sulphuric acid. When less concentrated sulphuric acid is used, for example, concentrations of 92% down to 85% H_2SO_4 it is desirable that a larger ratio of sulphuric acid to starting material be used, for example 15–25 parts of sulphuric acid to one part of terephthaloyl-ortho-benzoic acid.

The temperature of the step in which the treatment with nitric acid takes place is subject to variation between wide limits. Preferably a mixed acid comprising one part of HNO_3 and 2 parts H_2SO_4 is added to the reaction mass resulting from the first step (said reaction mass being diluted if necessary so that said reaction involves a 93–95% H_2SO_4 solution) at a temperature of 0°–5° C. over a period of one-half hour. The temperature is then allowed to rise slowly over one-half hour to room temperature, that is, to 25°–30° C. and then the charge allowed to stand for some time (for example, overnight). It has been found that the nitro group is introduced into the nucleus at about 15°–20° C. and that it is desirable, although not necessary, that the nitric acid be added slowly at any temperature near or below the temperature at which the introduction of the nitro group takes place. The best results have been obtained when the nitric acid was added at temperatures below 5°–8° C. No harm is done in raising the temperature after the addition of the nitric acid. Good results have been obtained with temperatures as high as 60°–80° C. However, there is a sacrifice of yield and quality when higher temperatures are used and as an outside range for best results the addition of nitric acid should take place at temperatures below 12° C. and the temperature should not be allowed to rise above 40° C. It is possible that the yield and quality may be adversely affected by heating for extremely long times even at 40° C.

In the procedure set out in Example II wherein the 1-nitro-anthraquinone-6-carboxylic acid filter cake was dissolved in dilute caustic alkali, for purification purposes the sodium salt of the 1-nitro-anthraquinone-6-carboxylic acid may be salted out at any temperature between 0° and 60° C. and with the concentration of the dissolved salt or salts (Na_2SO_4 or NaCl, KCl, etc) varying from 0 to 10%. No advantage is gained by using more than 8–10% salt concentrations when filtering the 1-nitro-anthraquinone-6-carboxylic acid alkali metal salt below about 25°–35° C. A higher concentration of salt does not seem to remove any more of the 1-nitro-anthraquinone-6-carboxylic acid alkali metal salt from the filtrate. At high temperatures proportionately higher concentrations of salt are advantageous.

In converting the alkali metal salt of 1-nitro-anthraquinone-6-carboxylic acid to the free acid it is sufficient to acidify to the point where the medium is acid to Congo red provided this concentration is maintained but preferably an excess of acid equal to 4 or 5 times that theoretically necessary to molecularly convert the salt to the acid is used as a safety factor. Under such conditions the concentration of the acid used for the conversion will be 1%–2% in the final mixture before filtration. Such a procedure assures complete conversion of the alkali metal salt to the free acid.

It is to be understood that it is not necessary to start with the 1-nitro-anthraquinone-6-carboxylic acid in order to produce the corresponding acid chloride. The alkali metal salt of the metal acid may be treated to produce the desired final product as indicated in Example IV.

For the purification of the 1-nitro-anthraquinone-6-carboxylic acid by use of alkaline solutions any of the alkalis for example NaOH, Na_2CO_3, KOH, K_2CO_3, NH_4OH, and the like may be used.

As will be clear from the above description of the invention, it is not limited to the preparation of 1-nitro-anthraquinone-6-carbonyl chloride. Any of the 1-nitro-anthraquinone-6-carbonyl halides may be produced by corresponding procedures.

While it is not desired to limit the invention to any particular theory, to aid in the understanding of the same, it may be stated that it is believed that the first step in the process in which the terephthaloyl-ortho-benzoic acid is treated with sulphuric acid results in the ring closure to an anthraquinone carboxylic acid. In any event during the second step of the process herein described, a nitro group is introduced into the molecule so that the nitro and carboxyl groups

are located at the 1 and 6 positions of the resultant anthraquinone nucleus respectively.

This invention has numerous advantages as will be clear to those skilled in the art after a consideration of the above described processes. Among these may be mentioned processes for preparing 1 - nitro - anthraquinone-6-carboxylic acid and its corresponding carbonyl halides by a novel, easily controllable, simple and direct series of steps. An extremely important advantage is that this invention provides a process for preparing the compounds in question which is not limited by narrow operating ranges of temperatures, pressures and proportions of components (narrow and delicate operating conditions are always disadvantageous in commercial practice).

In addition very valuable products are produced in desirable attractive commercially acceptable physical forms and in high purity. Other advantages which merit particular mention are excellent yields, elimination of the use of circuitous methods of preparation, and the like.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. As a new and useful chemical process the steps which comprise treating terephthaloyl-ortho-benzoic acid with sulphuric acid, treating the resultant product with a nitrating substance and treating the product with a substance capable of converting a carboxyl group to a carbonyl halide.

2. Process which comprises treating terephthaloyl-ortho-benzoic acid with concentrated sulphuric acid, adding a nitrating substance to the reaction mass, diluting resultant until a sulphuric acid concentration of 86% is obtained, filtering the solid material formed, washing the residue acid free, adding the washed residue to three parts of ortho-dichloro-benzene, distilling off the water present, cooling to 30° C., adding two parts of ortho-dichloro benzene containing phosphorus-pentachloride and separating the 1-nitro-anthraquinone-6-carbonyl-chloride formed.

3. As a new and useful chemical process the steps which comprise treating terephthaloyl-ortho-benzoic acid with sulphuric acid and treating the resultant product with a nitrating substance.

4. As a new and useful chemical process the steps which comprise treating terephthaloyl-ortho-benzoic acid with sulphuric acid, treating the resultant product with a nitrating substance and treating the product with a phosphorus pentahalide to convert the carboxyl group to a carbonyl halide.

5. Process which comprises treating terephthaloyl-ortho-benzoic acid with concentrated sulphuric acid, adding a nitrating substance to the reaction mass, diluting the resultant until a sulphuric acid concentration of 86% is obtained and filtering the solid material formed.

EARL EDSON BEARD.

CERTIFICATE OF CORRECTION.

Patent No. 1,985,232. December 25, 1934.

EARL EDSON BEARD.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 33, for "high" read higher; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of March, A. D. 1935.

Leslie Frazer

(Seal) Acting Commissioner of Patents.