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(54) A PROCESS FOR PRODUCING PHTHALIDE

(71) We, DYNAMIT NOBEL AKTIENGESELLSCHAFT, a German Company of 521 Troisdorf, bez Köln, Postfach 1209, Germany, 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:-

This invention relates to a process for producing phthalide by hydrogenolysis of 3-chlorophthalide.

Processes comprising the replacing of organically bound halogen atoms by hydrogen atoms, generally known as hydrogenolysis, in the presence of metallic palladium-,platinum- or nickel-containing catalysts are known. It is also known that in such processes, aromatically bound halogen atoms are more easily substituted than aliphatically bound halogens. In all cases, the less acidic the reaction solution, the more easily the reaction takes place. Since hydrogen halide, for example hydrogen chloride, is released during hydrogenolysis, hydrogen halide-acceptors, known *per se* are conventionally added to the reaction mixture in order to increase the reaction rate and the space-time yields.

Unfortunately, the addition of acid-binding compounds, for example amines, sodium acetate, or alkali metal methanolates, has the disadvantage of making the processing of the reaction product and of the catalyst considerably more difficult. In particular, the recycling of the catalyst essential to the process is only possible in some methods, meaning that a process using hydrogen halide-acceptors cannot always be applied industrially.

In reactions where chlorine atoms are being substituted, a further possibility of capturing the hydrochloric acid which is formed consists of carrying out the hydrogenolysis in the presence of a solvent which dissolves hydrogen chloride. Methanol, for example, is known to be suitable for use as solvent in the hydrogenolysis of benzyl chloride to toluene. However if methanol is used as solvent in an analogous process for producing phalide hy hydrogenolysis of 3-chloro-phthalide, it has been found that the initially formed phthalide reacts immediately with the hydrochloric acid present in the methanolic solution causing splitting of the lactone ring to form *o*-chloromethyl benzoic acid. This latter compound then reacts further with the methanol which is present in excess to form toluic acid methyl ester as one of the major products of the process. Indeed, phthalide has been found to be produced only in a yield of some 15 to 18%.

It has been found, too that even if 3-chlorophthalide is subjected to hydrogenolysis at for example 140°C, under pressure, in the absence of methanol, the above-mentioned lactone dissociation takes place, whereby the chloromethyl group is further broken down to the methyl group. The final reaction mixture then consists mainly of toluic acid together with a small amount of phthalide.

It is thus desirable to be able to conduct the hydrogenolysis of 3-chloro-phthalide in such a way that the formation of undesired by-products is repressed and yields of phthalide over 90% are generally obtained.

According to the present invention there is provided a process for producing phthalide comprising reacting 3-chlorophthalide and hydrogen at a temperature of from 50 to 250°C and in the presence of a hydrogenolysis catalyst, but in the absence of an acceptor for the hydrogen chloride produced during the reaction, to form the desired phthalide.

Preferably the reaction is carried out at a temperature of from 80 to 130°C, more preferably from 80 to 100°C,

Surprisingly, under the defined reaction conditions, and particularly in the preferred temperature range, the hydrogen chloride which forms only enters into secondary reactions to a minor extend during the time in which it is in the reaction mixture. The bulk of the hydrogen chloride formed is preferably immediately removed from the reaction mixture by a continuous through flow of hydrogen. Also, in the given temperature range, the acidic reaction medium which occurs has only a slight influence on the speed of the reaction.

The hydrogen is preferably added in such a quantity that it bubbles through the reaction mixture. Preferably, the mount bubbled through is at least 60 litres (at 25°C and 760 torr) per litre of reaction mixture. The hydrogen need not be specifically purified; it may have an industrial degree of purity throughout.

The catalyst need not be processed prior to re-use, since in carrying out the process of the invention insoluble chlorine compounds are formed. With a batch-type process the catalyst can be re-used immediately for the next batch, after the separation of the reaction product, without undergoing a special purifying operation. The activity of the catalyst has been found to be hardly diminished even after use in more than 20 batches.

The amount of catalyst present is preferably from 0.1 to 10% by weight, more preferably from 2.0 to 5.0% by weight, relative to the 3-chlorophthalide used. The precious metals in the VIII group of the 5th and 6th periods of the periodic system, which are also designated as platinum metals, for example rhodium, ruthenium or platinum, are preferred as catalysts. The metal may be used on a carrier, wherby the carrier preferably contains about 5% of the metal. However it is also possible to use carrier/catalyst systems with a higher or lower metal content. Carbon, aluminium oxide, barium sulphate of kieselguhr for example may serve as the carrier material The quantities of catalyst indicated above refer to the amount of catalyst carrier to be used, which contains the active metal. The periodic system referred to above may be found, for example, in Cotton and Wilkinson, "Advanced Inorganic Chemistry", Second Edition, 1966 (Interscience).

The reaction may be carried out either with or without solvent. Particularly preferred as solvents are those compounds which boil above 80°C and in which hydrogen chloride is only soluble to a slight degree. Obviously the solvent must be inert with regard to 3-chlorophthalide and phthalide and must allow these compounds to dissolve to a satisfactory degree. Aromatic hydrocarbons such as toluene or xylene may be used, for example.

If the reaction is carried out in the absence of solvents, the process must take place at a temperature above the melting point of phthalide. Preferably, the process is carried out at a temperature of from 80°C to 100°C.

It is preferred to carry out the process in an elongate, vertical reaction vessel, to the bottom of which is supplied fine bubbles of hydrogen. However, other reaction vessels may also be used provided that they ensure that the hydrogen is distributed throughout the entire reaction volume. As far as possible, the hydrogen supplied to the vessel should fluidize the catalyst in the reaction medium. In an elongate vertical reaction vessel, there is formed a column of liquid reactants with catalyst fluidized therein, which column is permeated by small hydrogen bubbles.

The hydrogen is passed through the reaction mixture until no more hydrogen chloride is evolved. The progress of the reaction may be followed by testing for hydrogen chloride in the gas mixture escaping from the reactor, which mixture is composed of excess hydrogen and the hydrogen chloride formed during the reaction.

After the completion of the reaction, the catalyst may be filtered off from the reaction mixture and the phthalide which has formed may be separated by conventional means, for example by distillation and/or crystallization.

The following Examples illustrate the invention. The parts referred to therein are parts by weight.

Example 1

842.5 parts 3-chlorophthalide were dissolved in 750 parts toluene in a bubble column 65 cm long and 6.5 cm in diameter, which bubble column was provided with a central delivery tube having perforated plates attached thereto. The bubble column was set into oscillation by means of a vibrator. In addition, there were present in the column 25.3 parts of a catalyst comprising an aluminium oxide carrier and 5% metallic palladium. With the solution at a temperature of 85°C, hydrogen was passed downwardly through the delivery tube at a rate of 120 litres per hour. The hydrogen was liberated from the delivery tube at the bottom and rose through the perforations of the perforated plates.

After separation of entrained vapours in a reflux condenser, the exhaust gas, comprising unreacted hydrogen chloride, was passed into a receiver in which a pH value of 7 was maintained by the continuous addition of standardized sodium hydroxide solution, so that in this way the progress of the reaction could be determined at any time.

After 6.25 hours, 99.8% of the theoretically obtainable HCl had been separated off and the formation of hydrogen chloride ceased. The solution in the bubble tube was separated from the catalyst and cooled to -10°C. 604 Parts phthalide (90.1% of the theoretical yield) were obtained, the melting point thereof being 72-73°C. The purity, as determined by gas chromatography, was 99%.

By further processing the mother liquor, another 40 parts phthalide of melting point 69-72, was obtained having a purity of 98%.

Example 2

In the same way as in Example 1, 842.5 parts 3-chlorophthalide were dissolved in 750 parts xylene. 25.3 Parts of catalyst comprising 5% Pd on Al_2O_3 were added and whilst maintaining the solution at a temperature of 115°C, 180 litres per hour of hydrogen were passed through the bubble column. After 1¾ hours, 98% of the theoretically obtainable HCl had been separated off. Hydrogen was passed through the tube for another thirty minutes, whereby the conversion was increased to 99.5% of the theoretical yield.

After separating off the catalyst, the remaining reaction mixture was distilled, and after removal of the first runnings of xylene, phthalide was distilled off at a pressure of 0.1 torr and a temperature of 103-106°C.

The yield of phthalide was 610 parts (91% of the theoretical) in the purity of 99.8%.

Example 3

842.5 parts 3-chlorophthalide were melted in an autoclave at 85C°, 25.3 parts catalyst (5% Pd on a carrier of $BaSO_4$) were added to the melt and, with strong agitation, a hydrogen flow of 180 litres per hour was passed through. Surplus hydrogen and the hydrogen chloride which formed were removed in the same manner as in the preceding Examples. After 8½ hours the formation of hydrogen chloride ceased and the molten mass was separated from the catalyst. 608 parts of phthalide (90.7% of the theoretical yield) was obtained by subsequent distillation, in a purity of 99.6%.

Example 4

842.5 parts 3-chlorophthalide and 750 parts xylene were heated to 85°C in a stirrer vessel with 25.3 parts of a catalyst comprising 5% Pt on a carbon carrier. With rapid stirring, 160 litres per hour of hydrogen was passed through the vessel. After a reaction time of 13 hours, formation of hydrogen chloride ceased and the catalyst was separated from the reaction mixture, which mixture was then processed by distillation. 549 parts of phthalide were obtained, corresponding to 81.9% of the theoretical yield.

Example 5

842.5 parts 3-chlorophthalide and 750 parts toluene were mixed, in the apparatus described in Example 1, with 25.3 parts of a catalyst comprising 5% Pd on Al_2O_3. With the reaction mixture at a temperature of 85°C, hydrogen was passed through the tube at a rate of 180 litres per hour. As soon as the generation of hydrogen chloride ceased, the catalyst was filtered off from the reaction mixture and the phthalide which had formed was separated by crystallization.

The filtered catalyst was returned to the apparatus, without further purification, together with 842.5 parts 3-chlorophthalide and 750 parts toluene, and the reaction was carried out again under the same conditions as before.

This procedure was repeated several times, and it is apparent from the following Table that the catalyst did not lose its activity even after numerous batches. Slight increases of the reaction times can probably be attributed to catalyst losses when the catalyst was filtered from the reaction mixtures. By adding small amounts of fresh catalyst, the original reaction time was re-established.

The series was discontinued after 22 batches, although the catalyst had still not lost its activity.

TABLE

Batch number	Reaction time (hours)	% yield of phthalide	Observations
1	5.5	94.5	
2	6.25	91.6	
3	6.0	90.1	
4	5.3	90.0	
5	6.3	88.4	
6	7.0	90.1	
7	7.2	92.0	
8	7.9	93.2	
9	7.9	92.1	
10	5.5	93.0	Addition of 2.0 parts of fresh catalyst
11	5.0	94.1	
12	5.5	92.7	
13	5.7	94.6	
14	5.9	95.0	
15	6.0	93.0	
16	6.5	92.5	
17	6.8	93.8	
18	7.0	90.0	
19	7.5	91.1	
20	7.7	89.2	
21	6.0	90.0	Addition of 1.5 parts of fresh catalyst
22	5.8	93.4	

WHAT WE CLAIM IS:-

1. A process for producing phthalide comprising reacting 3-chlorophthalide and hydrogen at a temperature of from 50 to 250°C and in the presence of a hydrogenolysis catalyst, but in the absence of an acceptor for the hydrogen chloride produced during the reaction, to form the desired phthalide.

2. A process according to claim 1 when carried out at a temperature of from 80 to 130°C.

3. A process according to claim 2 when carried out at a temperature of from 80 to 100°C.

4. A process according to claim 1, 2 or 3 when carried out in a liquid which is inert to the reactants and products and which is solvent for the 3-chlorophthalide and phthalide but substantially not for the hydrogen chloride which is formed.

5. A process according to claim 4 wherein the solvent is toluene or xylene.

6. A process according to any one of the preceding claims wherein the reaction is conducted by bubbling the hydrogen through the reaction mixture in an amount of at least 60 litres (measured at 25°C/760 Torr) per litre of reaction mixture.

7. A process according to any one of the preceding claims wherein the catalyst is present in from 0.1 to 10% by weight based on the weight of 3-chlorophthalide.

8. A process according to claim 7 wherein the catalyst is present in from 2.0 to 5.0% by weight based on the weight of 3-chlorophthalide.

9. A process according to any one of the preceding claims wherein the catalyst comprises a precious metal of group VIII of the 5th and 6th periods of the periodic classification of the elements (as hereinbefore defined).

10. A process according to claim 9 wherein the precious metal is platinium or palladium.

11. A process according to claim 9 or 10 wherein the catalyst consists of a metal supported on a carrier.

12. A process according to claim 11 wherein the carrier is carbon, aluminium oxide, barium sulphate of kieselguhr.

13. A process according to any one of the preceding claims and including the additional step of removing the phthalide from the reaction mixture.

14. A process according to any one of the preceding claims and including the further step of removing the catalyst from the reaction mixture.

15. A process according to claim 14 wherein the removed catalyst is re-used in another of said reactions.

16. A process according to claim 1 substantially as hereinbefore described in any one of the Examples.

17. Phthalide whenever produced by the process according to any one of the preceding claims.

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