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PRODUCTION OF ALIPHATIC DICHLORO COMPOUNDS

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The present invention relates to the production of aliphatic dichloro compounds and particularly to the preparation of 1.4-dichlorbutane and 4.4'-dichlordibutyl ether by the interaction of aqueous hydrochloric acid and tetrahydrofurane.

The synthesis of aliphatic dihalogen compounds is well known as, for example, the preparation of 1.4-dibrombutane from 1.4-dihydroxybutane or from ethers and esters thereof and hydrobromic acid. These processes have been considered of little interest for the commercial preparation of these compounds owing to the relatively small rate of conversion.

An object of the present invention is to provide an improved process for the synthesis of 1.4-dichlorbutane and at the same time to provide a simple process for the production of 4.4'-dichlordibutyl ether having the structural formula

$$ClCH_2CH_2CH_2CH_2OCH_2CH_2CH_2CH_2Cl$$

According to the present invention concentrated aqueous hydrochloric acid, i. e. hydrochloric acid containing at least 20 per cent of hydrogen chloride, is allowed to act on tetrahydrofurane at temperatures exceeding 100° C, preferably in the presence of catalysts promoting the formation of alkyl halides.

In order to effect the reaction as completely as possible, it is advantageous to work under superatmospheric pressure. The pressure employed should be so high that at least part of the tetrahydrofurane is in the liquid phase, the total pressure corresponding to the vapor pressure of all constituents of the reaction mixture at the reaction temperature. By employing inert diluent gases, such as nitrogen, the pressure may be increased beyond the pressure of the reactants, for example up to 50 or 100 atmospheres or even more. The pressure may also be increased by pressing anhydrous hydrogen chloride into the reaction vessel before or during the reaction.

The reaction proceeds with fairly satisfactory conversion already at temperatures between 110 and 140° C. The most suitable temperatures are within the range of 140 to 180° C. Temperatures exceeding 180° C cause the formation of higher molecular by-products and are not practicable.

The relative proportion of the reactants can be varied although it has been found that very advantageous results are obtained when the hydrochloric acid is in excess with respect to the tetrahydrofurane. In order to obtain a preponderating amount of 1.4-dichlorbutane, at least two molecular proportions or even more, e. g. 2.5 or 3 molecular proportions, of hydrochloric acid for each molecular proportion of tetrahydrofurane should be used. The proportion of 4.4'-dichlordibutyl ether in the reaction product may be increased by using from 1 to 2 molecular proportions of hydrochloric acid for each molecular proportion of tetrahydrofurane. Hydrochloric acid remaining unchanged and to be found in the final reaction mixture, will be found diluted by water formed in the reaction. It may be used again after having led in hydrogen chloride in order to obtain concentrated hydrochloric acid.

Catalysts may be employed in my process, though the conversion of tetrahydrofurane into 1.4-dichlorbutane and 4.4'-dichlordibutyl ether is already satisfactory without the aid of catalysts. Suitable catalysts are those which have proved useful for promoting the formation of alkyl halides from aliphatic alcohols or olefinic hydrocarbons and hydrogen halides, such as strong, non-oxidizing mineral acids, in particular concentrated sulfuric or phosphoric acid, and also metal halides, e. g. the chlorides of iron, bismuth, mercury, zinc or calcium, or iodine or activated carbon, silica gel and the like which may be impregnated with a metal salt of the type referred to above.

In the continuous preparation of 1.4-dichlorbutane and 4.4'-dichlordibutyl ether the use of concentrated sulfuric acid as catalyst has proved particularly useful.

A mixture of tetrahydrofurane and concentrated sulfuric acid to which concentrated hydrochloric acid has been added is heated in a closed vessel to temperatures within the range indicated above. From the resulting mixture 1.4-dichlorbutane and 4.4'-dichlordibutyl ether are distilled off. Hydrogen chloride is then led into the remaining mixture containing sulfuric acid, water, hydrochloric acid and unchanged tetrahydrofurane, thus strengthening the concentration of the hydrochloric acid. Further tetrahydrofurane is added and the reaction is again started.

This modification of my invention may be easily operated in a cycle by using as the medium and the catalyst for the reaction a mixture of sulfuric acid and water to which tetrahydrofurane and anhydrous hydrogen chloride in appropriate proportion are continuously added at the beginning of the vessel and from which the dichloro compounds are continuously withdrawn at the end of the vessel. At the end of the vessel and after having distilled off the dichloro compounds a small portion of the aqueous sulfuric acid is replaced by concentrated sulfuric acid in order to

maintain the concentration of the sulfuric acid present in the reaction.

When carrying out the process according to my invention with the aid of sulfuric acid, it is even possible to work at normal pressure, for example by allowing a mixture of tetrahydrofurane and aqueous sulfuric acid to flow through the vessel in counter-current to gaseous hydrogen chloride.

The following examples will illustrate methods of practizing the invention although the invention is not limited to the examples. The parts are by weight.

Example 1

A mixture of 120 parts of tetrahydrofurane, 164 parts of concentrated sulfuric acid and 440 parts of 38 per cent hydrochloric acid is heated under a pressure of 25 atmospheres to 150° C. in a vessel lined with lead for 4 hours. By distilling the reaction product under reduced pressure there are obtained 157 parts of 1.4-dichlorbutane and 20 parts of 4.4'-dichlordibutyl ether.

When heating a mixture of 120 parts of tetrahydrofurane, 164 parts of concentrated sulfuric acid and 350 parts of 33 per cent hydrochloric acid to 170° C. under a pressure of 15 atmospheres for 4 hours, there are formed 153 parts of 1.4-dichlorbutane and 22.5 parts of 4.4'-dichlordibutyl ether.

Example 2

150 parts of hydrogen chloride are led into a mixture of 360 parts of tetrahydrofurane, 60 parts of concentrated sulfuric acid and 630 parts of 38 per cent hydrochloric acid. The whole is heated in a pressure-tight vessel to 170° C. under a pressure of about 110 atmospheres for 4 hours. 354 parts of 1.4-dichlorbutane and 61 parts of 4.4'-dichlordibutyl ether are thus obtained.

Example 3

A mixture of 180 parts of tetrahydrofurane, 1000 parts of 38 per cent hydrochloric acid and 2.4 parts of bismuth trichloride are heated to 160° C. under a pressure of 30 atmospheres for 4 hours. 210 parts of 1.4-dichlorbutane and 20 parts of 4.4'-dichlordibutyl ether are thus obtained.

Example 4

160 parts of anhydrous hydrogen chloride are led into a mixture of 153 parts of 94 per cent tetrahydrofurane with 400 parts of 50 per cent sulfuric acid while cooling. The whole is heated in a pressure-tight vessel to 160° C. under 20 atmospheres pressure for 3 hours. The resulting mixture forms two layers, the aqueous layer consisting of sulfuric acid, water, hydrochloric acid and small amounts of tetrahydrofurane, the non-aqueous layer consisting of from 88 to 90 per cent of 1.4-dichlorbutane and from 10 to 12 per cent of 4.4'-dichlordibutyl ether. About 90 per cent of the tetrahydrofurane are thus converted. The aqueous layer may again be used for a new batch.

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