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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 hydrogen chloride 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 or esters thereof and hydrogen bromide: These processes have been considered of little interest for 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:

$$ClCH_2CH_2CH_2CH_2O.CH_2CH_2CH_2CH_2Cl$$

According to the present invention hydrogen chloride is allowed to act on tetrahydrofurane at temperatures exceeding 100° C under superatmospheric pressure. In order to effect the reaction as complete as possible, 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 reaction proceeds with fairly satisfactory conversion already at temperatures between 100° and 120° C. The most suitable temperature is within the range of 120° to 165° C. Temperatures exceeding 165° 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 hydrogen chloride is in excess with respect to the tetrahydrofurane. In order to obtain 1.4-dichlorbutane as the main reaction product, at least two molecular proportions or even more, e. g. 2,5 or 3 molecular proportions, of hydrogen chloride for each molecular proportion of tetrahydrofurane should be employed at temperatures between 140° and 165° C. The proportion of 4.4'-dichlordibutyl ether in the reaction product may be increased by using from 1 to 2 molecular proportions of hydrogen chloride for each molecular proportion of tetrahydrofurane at temperatures between 130° and 150° C.

The reaction may be carried out for example by charging liquid tetrahydrofurane into a pressure-tight vessel, pressing in anhydrous hydrogen chloride and then heating to reaction temperature. The hydrogen chloride may also be pressed in during or after heating the tetrahydrofurane. The formation of 4.4'-dichlordibutyl ether is particularly favoured when pressing in the amount of hydrogen chloride required for the reaction in small batches or in the form of a slow current into the hot tetrahydrofurane enclosed in a pressure-tight vessel.

Catalysts may be employed in our process, through the conversion of tetrahydrofurane into 1.4-dichlorbutane and particularly into 4.4'-dichlordibutyl ether is highly satisfactory without the aid of catalysts. Suitable catalysts are those which have proved suitable for promoting the formation of alkyl halides from olefines and hydrogen halides, such as metal halides, e. g. the chlorides of iron, bismuth, mercury, zinc or calcium, or iodine or active carbon, silica gel and the like which may be impregnated with a metal salt of the type referred to above.

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

Example 1

In a pressure-tight vessel made from steel of 1 liter volume 144 grams of tetrahydrofurane and 200 grams of anhydrous hydrogen chloride are heated at 150° C. for 5 hours. The reaction mixture is distilled, thus yielding 175 grams of 1.4-dichlorbutane corresponding to a yield of 70 per cent.

Example 2

In a pressure-tight lead-lined autoclave of 2 liters volume 700 grams of tetrahydrofurane and 2 grams of bismuth trichloride are heated to 160° C whereby a pressure of 15 atmospheres is reached. 725 grams of anhydrous hydrogen chloride are slowly pressed in, and the whole is kept at 160° C for 8 hours. By fractional distillation of the reaction mixture, there are obtained 1050 grams of 1.4-dichlorbutane and 100 grams of 4.4'-dichlordibutyl ether.

Example 3

Into a pressure-tight enamelled vessel of 30 liters volume there are charged 7 kilograms of tetrahydrofurane and 20 grams of bismuth chlo-

ride. 7.25 kilograms of anhydrous hydrogen chloride are pressed in and the whole is heated to 160° C for 5 hours. By fractionating the reaction mixture 11.6 kilograms of 1.4-dichlorbutane are obtained which corresponds to a yield of 94 per cent.

Example 4

7 kilograms of tetrahydrofurane are heated in a pressure-tight enamelled vessel of 40 liters volume to 140° C. In the course of 8 hours 5 kilograms of anhydrous hydrogen chloride are pressed in. When fractionating the resulting liquid, 1.7 kilograms of 4.4'-dichlordibutyl ether and 2.5 kilograms of 1.4-dichlorbutane are obtained. There is also formed some 1-chlor-4-hydroxybutane which can be easily reconverted into tetrahydrofurane.

Example 5

In a vessel as described in Example 4, 7 kilograms of tetrahydrofurane are heated to 115° C. 5.5 kilograms of the anhydrous hydrogen chloride are pressed in in the course of 8 hours. 1.65 kilograms of 4.4'-dichlordibutyl ether and 1.35 kilograms of 1.4-dichlorbutane are thus obtained. Part of the tetrahydrofurane is converted into 1-chlor-4-hydroxybutane.

Although the reaction is preferably carried out with the aid of pure, substantially anhydrous hydrogen chloride, since aliphatic dichloro compounds are produced in maximum conversion, the reaction may also be carried out with hydrogen chloride containing other gases, e. g. nitrogen or oxygen or water.

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