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PROCESS FOR PREPARING CYCLOPROPANE

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9 Claims. (Cl. 260—666)

This invention relates to the preparation of cyclopropane.

Cyclopropane has heretofore been prepared by the reaction of trimethylene dihalides with finely-divided metal reduction agents in various liquid reaction media (in whicl. the metal is suspended and the dihalide is more or less dissolved), e. g., by the reaction of trimethylene dibromide with zinc dust in aqueous ethanol. While this procedure has been developed to a high state of efficiency, the use of liquid reaction media gives rise to certain complications, inter alia, the (economic) necessity of recovering the medium if essentially alcoholic, and the occurrence of side reactions due to or involving the medium.

As described and claimed in the copending application of Christiansen and Ort, Serial No. 414,354, filed simultaneously herewith, cyclopropane can be prepared by contacting the vapor of a trimethylene dihalide with a metal reduction agent, a process which does not require the use of a liquid reaction medium.

The efficient operation of this process, however, requires the use of a large excess of the metal reduction agent to provide the necessary fresh (active) metallic surface, and consequently requires relatively large-capacity equipment. If the metal reduction agent is in finely-divided form and is stirred or agitated to increase the active surface presented within equipment of a given capacity, some of the metal reduction agent may thereby be carried into the condenser.

It is the object of this invention to provide an improved process of preparing cyclopropane which does not require the use of a liquid reaction medium or relatively large-capacity equipment.

The process of this invention essentially comprises intimately contacting a trimethylene dihalide—preferably in vapor form—with a liquid amalgam of a metal reduction agent. (The term "amalgam" is used herein in its recognized technical sense, i. e., as designating an alloy of mercury with another metal or metals.) The intimate contact may be effected by having the amalgam in particulate form, as by means of vigorous stirring. The amalgam is one either liquid at room temperature or liquefied by heating. Preferably, the metal reduction agent is used in excess to form an amalgam carrying (finely-divided) unamalgamated metal reduction agent.

The invention is applicable generally to the production of cyclopropane by the reduction of trimethylene dihalides; thus, the preferred trimethylene dihalides are the dibromide, chlorobromide, and dichloride, and the utilizable metal reduction agents include zinc, sodium, and magnesium. The reaction is favored by operating at elevated temperatures, a temperature of about 200–300° C. being optimal from the standpoint of obtaining a reasonably rapid reaction with a minimum of charring.

The process is conveniently carried out as follows: The reacting vessel is fitted with a device for vigorous stirring, a reflux condenser through which uncondensed gas (cyclopropane) can escape to a gasometer, and a device for drop-feeding the trimethylene dihalide; the temperature of the liquid amalgam is raised to well above the boiling point of the trimethylene dihalide used [any excess of the metal reduction agent present resting on the top of the amalgam]; the whole metal mass (both liquid and solid, if present) is stirred vigorously, so that particles of the liquid amalgam and finely-divided metal are dispersed throughout the interior of the reaction vessel; and the trimethylene dihalide is fed dropwise, whereupon it is vaporized and part of it reacts with the metal reduction agent, the unreacted trimethylene dihalide vapor being condensed and returned until consumed.

The following example is illustrative of the invention: 550 g. mercury is placed in a 3-neck 3-liter flask, and 300 g. zinc dust added. A stirrer is inserted through one of the necks, a thermocouple through another neck, and the third neck is connected to a reflux condenser and to a device for drop-feeding the trimethylene dihalide. The flask is then heated to 270–285° C., the stirrer operated rapidly, and 60 g. of trimethylene dichloride is fed dropwise over a period of an hour, meanwhile collecting the evolved cyclopropane; about 40 minutes thereafter, all liquid vanishes from the reflux condenser, and the reaction is complete. An approximately 75% yield of cyclopropane is obtained. The 300 g. zinc used is in great excess for the 60 g. trimethylene dichloride; and the excess zinc—and, of course, the mercury—are reused after cooling, removing the reaction-formed $ZnCl_2$ from the surface of the amalgam by washing with water, and adding more zinc dust to replace that used up in the reaction.

The use of trimethylene chlorobromide or trimethylene dibromide in lieu of trimethylene dichloride in the foregoing examples gives even better results; inasmuch as they are more reactive than the dichloride and hence do not require as high a reaction temperature, and the

use of lower temperatures minimizes side reactions and increases the yield.

Magnesium or other metal reduction agents may be used in lieu of zinc in the foreging example; and means other than those of the foregoing example may be used to effect intimate contact between the trimethylene dihalide and the liquid amalgam of a metal reduction agent.

The invention may be variously otherwise embodied, within the scope of the appended claims.

I claim:

1. The process of preparing cyclopropane which comprises intimately contacting a trimethylene dihalide with a liquid amalgam of a metal reduction agent.

2. The process of preparing cyclopropane which comprises intimately contacting a trimethylene dihalide with a liquid amalgam of a metal reduction agent at an elevated temperature.

3. The process of preparing cyclopropane which comprises intimately contacting the vapor of a trimethylene dihalide with a liquid amalgam of a metal reduction agent.

4. The process of preparing cyclopropane which comprises intimately contacting the vapor of a trimethylene dihalide with a liquid amalgam of a metal reduction agent at an elevated temperature.

5. The process of preparing cyclopropane which comprises contacting the vapor of a trimethylene dihalide with particles of a liquid amalgam of a metal reduction agent.

6. The process of preparing cyclopropane which comprises intimately contacting the vapor of a trimethylene dihalide with a liquid amalgam of a metal reduction agent, carrying unamalgamated metal reduction agent.

7. The process of preparing cyclopropane which comprises intimately contacting the vapor of a trimethylene dihalide with a zinc amalgam in liquid form.

8. The process of preparing cyclopropane which comprises intimately contacting the vapor of trimethylene dichloride with an amalgam of a metal reduction agent in liquid form.

9. The process of preparing cyclopropane which comprises intimately contacting the vapor of a trimethylene dihalide with a liquid amalgam of a metal reduction agent at a temperature of about 200–300° C.

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