Fig. 2.

RECEIVER FOR ABSORPTION OF HCl

RECEIVER FOR MESITYL OXIDE

CONDENSER

CONDENSERS

REACTION CHAMBER

CHLORINE IN

ACETONE

DRYER

RECEIVER FOR CHLOROACETONE

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2,235,562

METHOD FOR PRODUCING CHLORINATED KETONES

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Application September 1, 1938, Serial No. 228,007

5 Claims. (Cl. 269—503)

This invention relates to methods for a vapor phase chlorination of monochloroacetone.

The chlorinated ketones are used industrially for various purposes. For example, chlorinated acetone is a lacrimation. A number of methods have been described for the manufacture of chlorinated compounds. However, many of these involve the use of liquid phase conditions, discontinuous operation, or are otherwise less satisfactory than my novel procedure described herein.

I have discovered a method for chlorinating ketones, which method is adapted to relatively rapid continuous operation and is susceptible of control.

This invention has for one object to provide a method for chlorinating ketones. Still another object is to provide a method particularly adapted to the production of monochlor ketones such as monochloroacetone. Another object of this invention is to provide a process for the chlorination of ketones which is adapted to continuous operation. Still another object is to provide a process capable of producing chlorinated ketones contaminated with a minimum of unreacted ketone or other constituents. A still further object is to provide a process for the manufacture of chlorinated ketones including cooling, rectification, and other treatment of the product produced.

I have found that chlorine and ketone to be chlorinated may be readily and rapidly reacted in the vapor phase, the resulting chlorinated product being removed in the liquid condition and further treated as by cooling and rectification.

For a more complete understanding of my invention, reference is made to the attached drawings forming a part of the present application.

Fig. 1 is a semi-diagrammatic side elevation view of one arrangement of apparatus which may be used for carrying out my process.

Fig. 2 is another semi-diagrammatic side elevation view of apparatus in which certain parts have been modified, for carrying out chlorination treatment in accordance with my invention.

Fig. 3 is another apparatus set-up for carrying out my invention in which certain parts have been modified.

In the aforementioned figures some of the units have been shown on section or in exaggerated scale for clarity.

The drawings may be understood to a substantial extent from the legends appearing thereon. However, the following description is set forth with respect thereto.

Referring to Fig. 1, the apparatus there shown is comprised of a plurality of units 2, 3, 4, which are substantial duplicates of one another. Therefore, description will be confined mainly to one unit, particularly, unit 2.

Unit 2 is comprised of the reaction chamber 5, provided with a suitable chlorine inlet 6. The upper portion of the reaction chamber is connected by the vapor outlet tube 8 to a plurality of condensers 9, 11. These condensers are in turn connected to weir boxes, traps or the like, 12, 13 and feed into the outlet conduit 14 for acetone and the like.

The lower portion of the reaction chamber is provided with a ketone inlet 16 which is connected to a ketone reservoir 17. This ketone is either a cold or heated condition, by means of suitable connections 18, is introduced in close proximity to heated column 19, which, it will be seen as the disclosure proceeds, has for one of its functions the furnishing of gaseous ketone to the reaction chamber. This column is equipped with a liquid trap 20 and a draw-off conduit 21 leading to the receiver 22 for the chlorinated product.

The receiver for the crude chlorinated ketone, is adapted to supply the chlorinated ketone to a washer 24, a drier 26 and the rectification column 27.

Referring to Fig. 2, the parts there shown are somewhat similar to those already described. The apparatus is provided with a reaction chamber 31 into which feeds the chlorine inlet 32.

In the construction of Fig. 2, the ketone inlet 33 is positioned in the upper portion of the reaction chamber so that the inflowing ketone assists in condensing and carrying the chlorinated products out of the reaction chamber to the column 34, which column functions for vaporizing ketone back to the reaction chamber.

Column 34 is connected through liquid seal 36 to the receiver 37.

The reaction chamber, as in the apparatus of Fig. 1, is connected through a plurality of condensers 38, 39, 41 to receivers and collectors 42, 43 for mesityl oxide and hydrochloric acid, respectively.

The receiver 31 for the chlorinated product is adapted to supply a washer 44, drier 45 and rectifying column 46.

Referring to Fig. 3, a reaction chamber is provided at 51. However, in this apparatus arrangement the chlorine inlet 52 is positioned in the
vapor offtake passageway 53. This vapor offtake passageway is connected with a plurality of condensers 54 and 57 as already described.

The conduit 58 from the last condenser empties into suitable separatory means 59, including a plurality of columns 61, 62 for recovery of the various products carried out of the reaction chamber.

Positioned below the reaction chamber is ketone inlet 64, connected with the ketone vaporizer 55 and heated column 56.

As described with respect to the preceding figures, a column is provided at 66 for vaporizing ketone carried out in the reaction chamber. This column is connected through liquid seal 67 with the receiver 68.

The chlorinated products in the receiver may be drawn off through 75 to rectification apparatus or other equipment, as described with respect to the preceding figures.

The conduit 69 is provided for returning the chlorinated ketone to any chlorinated product which may have escaped through the upper portion of the apparatus.

Suitable recovery means for hydrogen chloride vapor may be provided at 70 and 71.

A plurality of devices, as chlorine cylinders, and associated parts, may be provided at 73 for furnishing the chlorinating medium.

It is to be understood that thermometers, suitable flow meters and other control devices may be inserted in the apparatus set-up wherever desired.

A further understanding of the operation of my novel apparatus as well as the functioning of my process will be apparent from the following examples. These examples are set forth primarily for the purposes of illustration and description of my preferred embodiment. Hence, it is to be understood that my invention is not to be restricted thereby.

Example I.—In accordance with this instance, I describe a run for making monochloroacetone.

The reaction may be indicated as follows:

\[
\text{CH}_2\text{COCH}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{CH}_2\text{COClCH}_2\text{Cl} + \text{HCl}
\]

In carrying out this preparation, apparatus setup such as disclosed in Fig. 1 is employed. The traps as at 21 were filled with acetone. Heat or cooling medium, as the case required, was supplied to the respective condensers and columns. The receiver 23 for the chloroacetone was externally cooled.

Acetone was run from the reservoir 17 into conduit 16, where upon emergence therefrom the acetone was vaporized by the steam-heated column 19. The acetone can be supplied in a relatively continuous steady stream, for example 2 liters per hour. This is sufficient to produce good refluxing and furnish ample acetone vapor to the reaction chamber shown. Chlorine is passed from suitable supply through the chlorine inlet 7 into the reaction chamber. Inasmuch as the monochloroacetone is desired, a too large quantity of chlorine is undesired. Approximately equimolar quantities of chlorine and acetone could be introduced into the reaction chamber. For example, in my apparatus, if sufficient chlorine is introduced to give a very slight greenish tinge to the reaction flask this indicates satisfactory supply.

Reaction takes place in reaction chamber 7 forming chloroacetones which immediately liquefy and flow into receiver 18.

The hydrogen chloride gas produced by the reaction leaves from the top of the reaction chamber and passes through the several condensers 8, 11, finally being withdrawn from unit 12 to absorption or other treatment. Acetone and other condensable constituents may be recovered at 14.

The chloroacetone containing some unreacted acetone, flows through column 13, trap 21 and conduit 22 into the cooled receiver 23. In the passage of the chloroacetone through the steam heated column 19, any acetone contained therein is vaporized back to the reaction chamber 5, thereby furnishing a gaseous ketone feed thereto.

The crude chloroacetone collected in receiver 23 may be periodically or continuously conducted to rectification for recovering monochloroacetone therefrom. In accordance with my preferred procedure, I interpose a washing and drying treatment prior to the rectification.

That is, the crude chloroacetone is treated with a saturated solution of sodium bicarbonate until neutrality is obtained. Thereafter the mixture is treated with calcium chloride with continuous stirring until two distinct layers are produced. The oily layer containing the bulk of the chloroacetone is separated, further dried and then subjected to rectification, as will be described. The salt solution may be discarded or further treated.

That is, the chloroacetone layer is preferably rectified under reduced pressure, using steam as the heating medium in a column provided with a water cooled still-head and water cooled receiver. The head product of the rectification was essentially comprised of monochloroacetone. The residue amounting to approximately 500 cc. comprised higher chlorinated products of acetone and may be saved, if desired. The monochloroacetone may then be further rectified by direct heating and a cut essentially comprising pure chloroacetone taken at between 117-120°C. The residue from this rectification may be returned to preceding steps in the process.

By my novel procedure, yields of chloroacetone amounting to 70% or more of the theoretical, may be obtained. This is largely monochloroacetone but a few percent of unsymmetrical chloroacetones may be present. The symmetrical chlorinated acetones may be more or less readily separated by my rectification procedure, hence, are not present.

Example II.—In accordance with the procedure of this example, which was carried out in an apparatus comparable to that described under Fig. 2, a certain amount of mesityl oxide was formed. That is, chlorine and acetone vapors were reacted in the reaction chamber 31. The temperature was maintained such that the chloroacetone formed immediately liquefied and flowed into column 34, where unreacted acetone was vaporized therefrom and returned to the reaction chamber for reacting with further chlorine.

The chloroacetone collected in receiver 37 and was subsequently treated as already described with respect to Example 1.

However, in this example, a certain amount of acetone was carried out of the apparatus into condensers 38, 39 and 41. This acetone in contact with some of the hydrogen chloride gas and chlorine therethrough, reacted quickly to form mesityl oxide. Other portions of the hydrogen chloride gas were absorbed in receiver 43.

The mesityl oxide so produced was agitation with sodium chloride and then neutralized with a solution of sodium hydroxide, using blue litmus as indicator. Suitable cooling accompanied this step. The oily layer was separated, washed with
water and then steam distilled. The oily layer resulting from this treatment was dried by stirring with calcium chloride and further distilled under reduced pressure to obtain mesityl oxide of a good quality.

Example III.—In accordance with the procedure in this instance, some excess chlorine was introduced into the reaction chamber. This is readily ascertainable by the dark green color of the reaction mixture when excess chlorine is present. The procedure was otherwise carried out more or less in accordance with that described with reference to Example I. However, the product collecting in the receiver comprised not only monochloroacetone, but dichloroacetones, such as symmetrical dichloroacetone.

The product so obtained was treated in the washer and drier as described and subjected to distillation in the still column 27. The head product from this distillation comprised monochloroacetone and the residue contained a substantial amount of symmetrical dichloroacetone. This s-dichloroacetone, together with water and calcium carbonate, was steam distilled and the oily distillate therefrom further distilled, cooled and filtered and otherwise treated for obtaining dichloroacetone crystals.

Example IV.—The apparatus arrangement employed in this example was that described in Fig. 3. The reaction was conducted substantially the same as described with respect to Example I. Acetone was fed into the vaporizer 65 where it was vaporized through column 55 and conduit 64 into the reaction chamber 51. Any acetone condensing in reaction chamber 51 is re-vaporized by the column 66, as already described in the preceding example. A suitable quantity of dried chlorine was introduced into the reaction chamber through conduit 52. As already indicated, if too much chlorine is added the reaction chamber tends to become dark green and chlorine is lost through the condenser. However, if too little chlorine is added, there will be a condensing of the steam column 65 and losses of acetone through condensers 54 and 57.

The chloroacetone formed in this example flows through the liquid seal 67 into the receiver 68, from which it was withdrawn for rectification and other treatment already described in the preceding examples.

However, by the arrangement shown in Fig. 3, unreacted acetone and chloroacetone, which escapes with the hydrogen chloride gas, may readily be recovered and returned to the system. The hydrogen chloride vapors may be drawn off through conduit 10 to a suitable receiver. The acetone passes into the vaporizer 65. Separation of the aforementioned constituents is accomplished merely by maintaining the temperatures in the respective condensers such that the acetone is condensed but the hydrogen chloride remains in the gaseous condition. By means of the steam heated column 62, any chloroacetone passing therethrough becomes heated and volatile constituents, as acetone, are removed therefrom.

Also, in the arrangement disclosed in Fig. 3, while the acetone is supplied to the reaction chamber in the gaseous state in a manner similar to that described in Fig. 1, a portion of the vaporization load is taken off column 66 by means of the vaporizer 65. Yields comparable to those described with respect to Fig. 1 are obtained by this modified procedure.

By my novel process it is possible to obtain relatively high yields of chlorinated ketone products of good quality. My processes and apparatus may be used in manufacturing various chlorinated ketones and is particularly adapted for the continuous vapor phase manufacture of chlorinated acetone, because of the volatile nature of acetone. My novel process is relatively simple and efficient in operation, lending itself to control, whereby the monochlorinated product, or, for example, 10 the dichlorinated products may be obtained as described. The various chlorinated products are rectified and preferably otherwise treated as described. Although I have disclosed the use of treating agents such as sodium carbonates, calcium chloride or the like, various other alkali carbonates or alkali materials may be employed or other hygroscopic salts other than calcium chloride used in the drying step.

As already indicated, I have provided a novel apparatus arrangement which may be caused to function continuously with a minimum of effort, producing high quality products in simple and efficient manner.

It is therefore apparent from the preceding that my invention is susceptible of some modification. Therefore, I do not wish to be restricted excepting insofar as is necessitated by the prior art and the spirit of the appended claims.

What I claim and desire to be secured by letters Patent of the United States of America is:

1. A continuous process of chlorinating aliphatic ketones which comprises introducing chlorine and a gaseous ketone into a reaction chamber, substantially continuously removing the product in liquid condition as soon as reaction has occurred, immediately passing the product through a heated vertical rectifying column, whereby at least a portion of the constituents, volatile at the temperature of the column, are removed and directly returned to the reaction chamber, and collecting the chlorinated product at the bottom of said column in a cooled chamber.

2. A process for the manufacture of chlorinated ketones, which comprises reacting in the vapor phase ketone with chlorinating agent, immediately passing the chlorinated ketone reaction product in liquid condition through a heated column at a temperature sufficient to volatilize back to the reaction chamber any unreacted component contained therein, further cooling the chlorinated ketone and subjecting it to further treatment including washing, drying, and rectification.

3. A process for the manufacture of chloroacetone and mesityl oxide, which comprises reacting chlorine and acetone in the vapor phase to obtain chloroacetone, and hydrogen chloride vapors, bringing said hydrogen chloride vapors into reactive contact with acetone, whereby mesityl oxide is formed and cooling the resultant mesityl oxide.

4. A process for the manufacture of symmetrical dichloroacetone, which comprises reacting in the vapor phase, acetone and sufficient chlorine to displace at least two hydrogen atoms in said acetone molecule, immediately withdrawing from the reaction in the liquid phase, chloroacetones produced, subjecting these liquid chloroacetones to heating, whereby any unreacted acetone therefrom is volatilized and subjecting the chloroacetones to further treatment for the separation of symmetrical dichloroacetone.

5. A process for the manufacture of chlorinated ketones, which comprises reacting in the vapor phase acetone and chlorine.
phase ketone with chlorinating agent, substantially immediately passing the reaction product and any unreacted ketone into a heated column at a temperature sufficient to volatilize unreacted ketone, whereby at least a part of any unreacted ketone therein is caused to be returned to the reaction chamber, withdrawing from the column chlorinated ketone from which unreacted ketone has been separated, and subjecting this chlorinated ketone to further treatment including washing, drying, and rectification.

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