

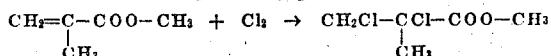
**2,320,034**

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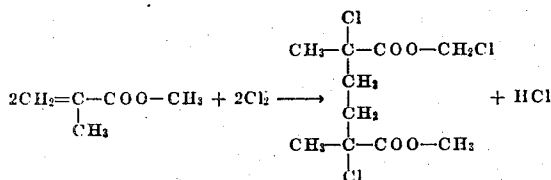
**4 Claims. (Cl. 260—487)**

chloro compound was obtained in preponderant amount and the residue, presumably the dimer, was much reduced in quantity.

To illustrate the method, the following example is given but it will be understood that the invention is not limited to the details therein given. Chlorine was passed into 400 ml. of chloroform, which was cooled in an ice bath and there was then added dropwise with stirring 100 grams of methyl methacrylate, the addition requiring about two hours. When starting the addition of the ester, the ice bath was lowered and the temperature of the chloroform allowed to rise to about 25–30° C., at which point it was kept by occasional cooling. The flow of chlorine into the reaction medium was maintained during the ester addition so that an excess of chlorine was present at all times. When a permanent chlorine color had been attained, the reaction product was fractionated and there was obtained a yield of 126 grams, or 74%, of the desired methyl alpha, beta-dichloroisobutyrate. The product had a boiling point of 95–100° C. at 55 mm., an index of refraction of  $n_D^{25}$  1.4495, and a density of  $D^{25}$  1.243. The molar refraction  $MR_D$  was 36.9; calculated for  $C_5H_8O_2Cl_2$ , 36.8. The residue, probably was dimer, amounted to 36 grams.



and the production of the dimer probably results from the following reaction:



It is an object of the present invention to improve the yield of the desired dichloro compound with a corresponding reduction in the amount of dimer which is produced. A further object is to extend the method to the treatment of esters of unsaturated acids of a type similar to the acrylates, that is to the halogenation of compounds which may be considered to be esters of beta hydrocarbon substituted acrylic acids. The reaction, as previously applied to the chlorination of methyl methacrylate, involves the addition of chlorine or other halogen to the acrylic ester and it was observed that an excess of the ester was present. This excess of ester is believed to favor the production of dimer at the expense of the desired product. Accordingly, the present method is characterized by the maintenance of an excess of the other reactant, the halogen, at all times during the course of the reaction, one method of accomplishing this being to saturate an appropriate reaction medium with the halogen and then add the ester to this saturated medium gradually while still continuing to add more halogen. In this way, the halogen is always present in excess of the ester. The results obtained fully confirm the theory since the di-

The method is of course applicable to the preparation of other esters of dihalocarboxylic acids 30 such as the esters of alpha, beta-dichloropropionic acid, alpha, beta-dichlorobutyric acid, alpha, beta-dichlorocaproic acid, alpha, beta-dichloroisocaproic acid, alpha, beta-dibromoisobutyric acid, diiodoisobutyric acid, and the alpha, 35 beta-dihalo, beta-methyl butyric acids. Other important esters are those of oleic acid and undecylenic acid, which are commercially available. The alcohol radical of the ester may be alkyl, such as methyl, ethyl, propyl, isopropyl, butyl, 40 isobutyl, amyl, isoamyl, cyclohexyl, cyclopentyl, chloroethyl, bromoethyl and chloropropyl or it may be aryl or aralkyl, such as phenyl benzyl, alpha naphthyl, beta naphthyl, xenyl, phenethyl and the like. As indicated, other halogens may 45 be added in place of chlorine in the formation of esters related to those above mentioned, bromine and iodine being added in a similar manner.

The conditions of the reaction are such as will permit the maintenance of an excess of halogen in the reaction medium, the temperature being maintained between 0 and 50° C. but preferably in the neighborhood of 20–30° C. A suitable medium will be present to contain the halogen, chloroform being one but carbon tetrachloride, dichloroethane, CS<sub>2</sub>, acetic acid and other sol-

vents for halogen also being suitable. The reaction medium should also be a solvent for the ester for best results, although this is not strictly essential. A halogenation catalyst may be used to promote the reaction, for example, ferric chloride, stannic chloride, iodine and the like. It is also desirable to have present a polymerization inhibitor.

While there have been described above the preferred embodiments of the invention, it will be apparent to those skilled in the art that various modifications and changes may be made therein without departing from the spirit of the invention or from the scope of the appended claims.

I claim:

1. A method of preparing methyl alpha, beta-dichloroisobutyrate which comprises saturating chloroform with chlorine and then adding methyl methacrylate gradually to the solution while passing additional chlorine into the chloroform.

2. A method of preparing esters of dichloro carboxylic acids which comprises chlorinating an alkyl ester of the class consisting of the acrylates and the alpha alkyl-substituted acrylates

while in solution and maintaining in the solution throughout the chlorination an excess of chlorine over that required to react with the ester.

3. A method of preparing esters of dichloro carboxylic acids which comprises passing chlorine gas into a solvent to build up a substantial concentration of chlorine therein and then dissolving therein an alkyl ester of the class consisting of the acrylates and the alpha alkyl-substituted acrylates and passing chlorine into the solution so that throughout the chlorination there is an excess of chlorine in the solution over that required to react with the ester.

4. A method of preparing esters of dichloro carboxylic acids which comprises saturating chloroform with chlorine and then gradually adding to the resulting solution an alkyl ester of the class consisting of the acrylates and the alpha alkyl-substituted acrylates while passing additional chlorine into the solution so as to maintain in the solution throughout the chlorination an excess of chlorine over that required to react with the ester.

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