10

35

UNITED STATES PATENT OFFICE

2,176,181

METHOD OF MANUFACTURING ORGANIC CHLORINE AND BROMINE DERIVATIVES

Heinz Hunsdiecker, Cläre Hunsdiecker, and Egon Vogt, Cologne-Lindenthal, Germany

No Drawing. Application April 2, 1936, Serial No. 72,446. In Germany April 8, 1935

9 Claims. (Cl. 260-487)

In the German periodical Monatshefte fuer Chemie, vol. 14, page 88 et seq. Simonini describes a process in which iodine, reacting with the silver salts of fatty acids yields a product which upon heating, changes into CO₂.AgI, and an ester R.COO.R in which R represents the hydrocarbon group of the fatty acid.

One might expect a similar reaction if chlorine and bromine were substituted for the iodine.

As appears, however, from the method forming the subject-matter of the present invention, the reaction of the silver salts with chlorine or bromine proceeds completely differently, viz. according to the following equation:

$R.COO.Ag+Br_2=R.Br+CO_2+AgBr$

There are, thus, obtained from fatty acid silver salts and chlorine or bromine, and with the splitting-off of a C-atom, besides AgCl, or AgBr respectively, the alkyl-halides. The reaction is not restricted to the silver salts; it proceeds in the same manner also with numerous other metal salts, especially with those of the first, the second, and the third group of the periodic table of the elements.

Also the salts of substituted fatty acids react in a similar manner, in which cases always compounds poorer by one C-atom are formed.

Thus, from α hydroxy-acids, hydrogen halide **30** compounds of the aldehydes are obtained:

$R.CHOH.COOMe + Hlg_2 \rightarrow$

R.CHOH.Hlg+CO₂+MeHlg

From hydroxy-acids in which the hydroxyl so group is not in the α position, hydroxy-alkylhalides are obtained:

$\textcolor{blue}{\textbf{HO.R.COOMe+Hlg_2\rightarrow HO.R.Hlg+CO_2+MeHlg}}$

From polyhydroxy-acids with one OH-group in the alpha position are obtained the hydrogen halide compounds of the hydroxy-aldehydes:

$(OH)_n$.R.CHOH.COOMe $+Hlg_2 \rightarrow$

(OH) n.R.CHO.HHlg+CO2+MeHlg

From α-halogen-fatty acids are obtained 1,1-halogenated hydrocarbons:

R.CHHlg.COOMe+Hlg2-R.CHHlg2+CO2+MeHlg

From n-fold halogenated fatty acids are obtained the (n+1)-fold halogenated hydrocarbons:

$Hlg_n.R.COOMe + Hlg_2 \rightarrow Hlg_n.R.Hlg + CO_2 + MeHlg$

From dicarboxylic acids are obtained di-substituted hydrocarbon-halides: R.(COOMe)2+2Hlg2→R.Hlg2+2CO2+2MeHlg

From ester-acids are obtained the halogen-fatty-acid-esters:

From α -keto-acids are obtained the acid halides (poorer by 1 C-atom):

$R.CO.COOMe + Hlg_2 \rightarrow R.COHlg + CO_2 + MeHlg$

From cycloalkan-mono- and -polycarboxylic acids are obtained the corresponding cycloalkylhalides, for example:

$$\begin{array}{c} \text{CH}_2 \\ \text{CH}_3 \\ \text{CH}_4 \\ \text{CH}_2 \\ \text{CH}_5 \\ \text{CH}_6 \\ \text{CH}_7 \\ \text{CH}_8 \\$$

From amino-acids (except α -amino-acids) are 25 obtained the halogen-alkylamines:

NH₂.R.CO₂Me+Hlg₂=NH₂.R.Hlg+CO₂+MeHlg

And from α -amino-acids are obtained the alkylidene-imine-hydrohalides which, with H_2O , 30 decompose into aldehydes, viz:

(1) R.CHNH₂.COOMe+Hlg₂→

R.CH:NH.HHlg+CO₂+MeHlg.

(2) R.CH:NH.HHlg+H₂O→R.CHO+NH₄.Hlg.

The following examples will serve to illustrate fully the present invention:

(1). 1 mol of well-dried silver palmitate is exposed to a current of air having a temperature of 30 to 50° C. and being laden with bromine vapor, this process being continued until no bromine is any more absorbed. From the pasty mass the pentadecyl bromide is obtained by subjecting the mass to pressure, or what is to be preferred, said bromide is extracted by means of ether or the like, and if desired, it may easily be purified by distillation under vacuo. The yield amounts to about 75 to 80% of the theoretical.

(2). 1 mol of well-dried silver laurate is transfromed into pasty state with CCl4, and simultaneously therewith, or thereafter, I mol of Br2 is gradually added, the mixture being now and then cooled. The further working is then effected in the same manner as in the preceding 55

example. Instead of CCl. also CHCl. or dry ether may be used. The yield in undecyl bromide amounts to about 75 to 80% of the theoretical.

(3). 1 mol of silver acetate is subjected in a suitable vessel to a current of air saturated with bromine vapor, care being taken that the temperature in the reaction vessel does not become too high. The escaping gases are, by means of CuCl or the like, freed from the excess of the bromine, and the methyl bromide thus obtained is condensed in a well-cooled receiver. The yield in methyl bromide amounts to about 80% of the theoretical.

(4). Coco fat is saponified with the just sufficient quantity of dilute alcoholic sodium hydroxide, whereafter the silver salts of the coco oil fatty-acids are precipitated by means of nitrate of silver, said salts being then washed and dried. The further procedure is carried out in the same manner as in the examples 1 and 2, whereby finally as product a mixture of alkyl bromides or carbon-chains C7—C17 is obtained.

It is in this case particularly remarkable that one succeeds in this way, starting from carbonchains with an even number of C-atoms, to obtain alkyl-halides with an odd number of C-atoms. These compounds do not exist in nature, they are not in natural products, and the chemical industry has hitherto been compelled to omit their utilization, but owing to the new conversions above disclosed this is no longer necessary, as, starting from the alkyl-halides, it is easily possible to obtain numerous important compounds. Besides, the metals are very easily quantitavely regenerable.

(5). 10 grams of the silver salt of α-hydroxy-palmitic acid are treated with bromine, as in the examples 1 and 2. After separation by means of ether, the hydrobromide of the pentadecylaldehyde which was obtained according to the equation:

CH₃.(CH₂) ₁₃.CHOH.COOAg+Br₂→ CH₃.(CH₂) ₁₃.CHO.HBr+AgBr+CO₂.

can easily be converted into a phenyl-hydrazone and separated as such.

(6). 20 grams of the silver salt of α -bromostearic acid are subjected to bromine in CCl₄ at a possibly low temperature until an action and a splitting-off of CO₂ does no more take place. The The ethereal extract is shaken with a solution of NaHCO₃ and then concentrated by evaporation. The yield amounts to about 12 to 13 grams of 1,1-dibromo-heptadecane.

(7). 20 grams of the silver salt of the 9,10-dichloroctadecanoic acid (obtained from chlorinated oleic-acid) are well dried and pulverized finely during a comparatively long time in a mechanical mortar. Then a solution of bromine in CCl4 is added until no bromine is any more taken up. After having filtrated and concentrated by evaporation 1-bromo-8,9-dichloroheptadecane is obtained in the form of a darkly-colored product. Yield: 13 grams.

(8). 37 grams of well-dried and pulverized silver sebacate are introduced by and by into a solution of 29 grams of bromine in dry CCl4, the liquid becoming hot by itself and commencing to scum, so that it must now and then be cooled.
The reaction product is extracted, the extract is concentrated by evaporation, and distilled under vacuo.

Yield: 15 grams. bp. 140-144° C. at 15 mm.

(9). To 217 grams of the silver-salt of the 75 sebacinic-mono-ethyl-ester-acid are added 110

grams of bromine, as in the preceding examples. There are obtained 126,5 grams (-75% of the theoretical) of 9-bromo-nonyl-acid ethyl-ester. Boiling-point: 118° C. at 2 mm. Hg.

(10). 10 grams of the silver salt of pyruvic acid are carefully and with very good cooling, mixed with a solution of bromine in CCl4 until no bromine is any more bound. The acetyl bromide obtained according to the equation

CH₃.CO.COOAg+Br₂→CH₃.CO.Br+CO₂+AgBr can be separated from the CCl₄ only with difficulty, and it is, therefore, preferably used to-

gether with it for acetylizations.

(11). 26 grams of silver mandelate are carefully and gradually mixed in dry ether with 15 grams of bromine, whereafter the ether is separated and the remaining product is concentrated by evaporation. The benzaldehyde obtained according to the formula

C6H5.CH.OH,COOAg+Br2→

C₆H₅.CHO.HBr+CO₂+AgBr

is preferably purified by the bisulfite compound. The yield varies, in that the hydrogen bromide arising at the same time splits partly the silver salt.

(12) 7.5 grams of glycocol are thoroughly intermixed by rubbing with 21.6 grams of precipitated HgO so as to obtain a product, the essential component of which is mercury amino acetate. Then a 10% solution of bromine in carbon disulphide is gradually added as long as bromine is still consumed. There escapes a regular current of CO₂ and of formaldehyde. The yield in formaldehyde amounts to about 60 to 80% of the theoretical.

(13). 1 mol of silver stearate is subjected to the action of dry chlorine at a gradually rising temperature (twards the end 100° C.). It is suitable to the purpose in view to interrupt the procedure from time to time, and the mass finally obtained is then thoroughly kneaded. After the pasty mass has been extracted with ether the resulting product consists nearly entirely of heptadecyl chloride. The yield depends greatly on how well one succeeds in subjecting the entire quantity of the silver stearate possibly quickly to the action of the chlorine.

(14). 50 grams of mercurous caprylate are mixed, at a temperature of about 60 to 80° C., with a solution of 35 grams of bromine in 100 ccm. of CCl4. The CO₂ splitting-off takes place somewhat slower than with the silver salts. The mercurous and mercuric-bromide obtained by the then following filtration is shaken repeatedly with hot water, and there is finally obtained heptyl bromide of excellent purity. Yield: 14–16 grams.

(15), 75 grams of well-dried mercuric palmitate are moderately heated and mixed in this 60 state with a mixture of 40 grams of bromine in 150 ccm, of CCl4. When the CO2-disengagement has ceased, the composition is still heated for a short period of time in a water-bath and is finally filtered and concentrated by evaporation. While this takes place, there separate mercurycontaining impurities, from which can be decanted, in order to remove further impurities, the product is distilled under vacuo. It is also possible to heat it together with pyridine for from 70 1 to 2 hours at a temperature of from 100 to 110° C., then dissolve it in a small amount of alcohol, and precipitate a pyridinium salt by means of an excess of ether. This salt contains then the entire amount of the pentadecylbromide in the 2,176,181

3

form of pentadecyl-pyridinium-bromide. Yield:

60-70% of the theoretical.
(16). Thallous heptylate is prepared by concentrating by evaporation an aqueous solution of 1/10 mol of hydroxide of thallium and 1/10 mol of heptylic acid. The thallium product thereby obtained is treated with chlorine or bromine, as in some of the preceding examples, there being then obtained hexyl chloride, or hexyl bromide 10 respectively, in a yield amounting to nearly 100% and being easily separable from the thallium halides by distillation.

(17). 102.5 grams of mercuric caprylate mixed 100 ccm. of CS2 are further mixed gradually in 16 a flask equipped with a reflux condenser with 22 ccm. of Br2. There arises a uniform current of CO2. After the conversion has become complete the separated HgBr2 obtained by filtration is thoroughly washed with CS2. The carbon di-20 sulfide is distilled off with the aid of a waterbath, and the residue is fractionated under vacuo. There are obtained 55.7 grams of heptyl bromide having a boiling point of 74° C., said amount being 75.5% of the yield in bromide theo-25 retically to be expected.

(18). 41 grams of dodecandicarboxylic acid are mixed with 100 ccm. of CCl4, and then 9 ccm. of bromine are gradually added. After the reaction has been finished, the silver bromide is sepa-30 rated by filtration and washed out with hot CCl4. The filtrate is freed from the excess of bromide and of small amounts of acid by being shaken with a solution of NaHCO3 is concentrated by evaporation, and the residue is distilled under 35 vacuo. There are obtained 16.8 grams of 1.12dibromo-decane having a boiling point of 190-195° C. and a fusing point of 35 to 36°, said amount of grams being equal to 60% of the theoretical.

We claim:

1. The method of manufacturing halogencontaining organic compounds from organic substances containing carboxyl groups, said substances being salts of metals selected from the ## group consisting of mercury, silver and thallium, said method comprising reacting upon said selected salt in the absence of water, with a halogen chosen from the group consisting of chlorine and bromine in gaseous form, whereby CO2 and 50 a metal halide splits off and a mono-halogenated hydrocarbon remains.

2. The method of manufacturing organic halogen-containing compounds which comprises reacting, in the absence of water, a metal salt of 55 a saturated fatty acid where the metal is a member of the group consisting of silver, mercury and thallium, with a substance chosen from the group which consists of chlorine and bromine, whereby the carboxylic group splits off and is re-⁸⁰ placed by a single halogen atom.

3. The method which comprises reacting, under anhydrous conditions, a halogen of the group consisting of bromine and chlorine upon a saturated fatty acid compound which contains at 65 least one —CCOZ group, wherein Z is a member of the group consisting of mercury, thallium and silver, whereby at least one COOZ group is replaced by not more than a single halogen atom.

4. The method which comprises reacting, un-70 der anhydrous conditions, a halogen of the group consisting of chlorine and bromine upon a saturated fatty acid compound which contains at least one —COOZ group, wherein Z is a metal chosen from the group which consists of silver. mercury and thallium, whereby carbon dioxide 5 and a metal halide split off, and leave a monohalogenated hydrocarbon.

5. The process of manufacturing saturated alkyl halogen compounds containing an odd number of hydrogen atoms which comprises subject- 10 ing a dry silver salt of an a-hydroxy carboxylic acid, whose alkyl group contains an even number of hydrogen atoms to the action under anhydrous conditions of a halogen chosen from the group consisting of bromine and chlorine 15 until carbon dioxide ceases to escape, whereby the carboxyl group splits off and is replaced by a single halogen atom.

6. A process of manufacturing organic halogen compounds from saturated carboxyl containing 20 salts chosen from the group consisting of silver, mercury and thallium salts, under anhydrous conditions, which process comprises saturating said salts with a halogen chosen from the group consisting of bromine and chlorine whereby a 25 metal halide is formed and one carboxylic group is replaced by one halogen atom to form a monohalogenated hydrocarbon and separating and purifying said halogenated compound.

7. A method of manufacturing halogen-con- 30 taining organic compounds from saturated carboxyl-containing salts of metals chosen from the group which consists of silver, mercury and thallium, which comprises completely reacting said salts under anhydrous conditions with a halo- 35 gen chosen from the group consisting of chlorine and bromine, whereby carbon dioxide and metal halide split off and are replaced by a single atom of halogen, thus forming a halogenated hydrocarbon.

8. The method of manufacturing halogen-containing organic compounds from organic substances containing carboxyl groups, said substances being salts of metal selected from the group consisting of silver, mercury and thallium, $_{45}$ said method comprising completely reacting upon said selected salt under anhydrous conditions. with a solution of a halogen selected from the group consisting of bromine and chlorine, dissolved in a solvent chosen from the group consisting of ether, carbon di-sulfide and carbon tetrachloride, whereby the carboxyl group is replaced by a single atom of halogen, whereby a halogenated hydrocarbon is formed.

9. The method of manufacturing halogen-con- 55 taining organic compounds which comprises reacting, under anhydrous conditions, salts of the metals chosen from the group which consists of silver, mercury and thallium combined with acids selected from the group consisting of hy- 60 droxy fatty acids, poly-hydroxy fatty acids, α-keto fatty acids, α-halogen fatty acids, polyhalogen fatty acids, dicarboxylic fatty acids. acyloxy fatty acids, cyclo-alkyl mono- and polycarboxylic acids and amino fatty acids thereby 65 splitting off at least one carboxylic group and replacing it by one halogen.

> HEINZ HUNSDIECKER. MRS. CLÄRE HUNSDIECKER. EGON VOGT.

70