

monoethanolamine slowly added. The mixture was refluxed for four hours and on cooling deposited yellow crystals. Recrystallizations from butanol yielded the oxazolidine, m. p. 169°.

The other oxazolidines were made in a similar manner and are reported in Table I. Butyl ether or a mixture of butyl ether and butanol may be used as solvents and after refluxing, removed under vacuum.

Summary

1. An improved method for making substituted phenyl oxazolidines is reported.
2. Salicylic aldehyde and *o*-chlorobenzaldehyde, due to chelation, form addition compounds instead of oxazolidines.

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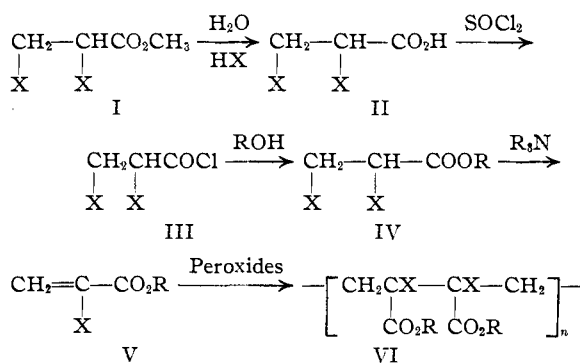
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polymers of the α -Haloacrylic Acids and their Derivatives¹

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Despite general recognition of the fact that substitution of halogen for hydrogen in a vinyl group usually accelerates the speed of polymerization, interest in the poly- α -haloacrylates has been dormant until recently. The discovery⁴ that the polymers of methyl α -chloro- and α -bromoacrylates have the "head to head, tail to tail" structure has stimulated further work on the haloacrylic acids and their acid chlorides and esters in order to learn their propensity to polymerize and the nature of the polymers.

The starting materials used in our work were methyl α,β -dichloropropionate and methyl α,β -dibromopropionate which were conveniently prepared by the addition of halogen to technical methyl acrylate. These esters have long been known^{5,6} but the present preparative procedures have apparently not been described before. The alkyl haloacrylates (V) were prepared from the methyl dihalopropionates (I) by the following steps



(1) This is the tenth communication on vinyl polymers. For the ninth see THIS JOURNAL, **62**, 2666 (1940).

(2) Du Pont Special Research Assistant in Chemistry, 1940.

(3) Du Pont Special Research Assistant in Chemistry, 1938-1939.

(4) Marvel and Cowan, THIS JOURNAL, **61**, 3156 (1939).

(5) Franklin and Turnbull, *J. Chem. Soc.*, **105**, 459 (1914).

(6) Moureu, Murat and Tampier, *Ann. chim.*, **15**, 221 (1921).

To obtain the phenyl ester (IV, R = C₆H₅) the acid chloride (III) was treated with phenol and pyridine. Removal of halogen acid from the dihaloesters (IV) was conveniently accomplished with such amines as quinoline, quinaldine or dimethylaniline. α -Chloroacrylyl chloride was obtained from α,β -dichloropropionyl chloride by heating with dimethylaniline.

The esters of the α -haloacrylates studied were the ethyl, *s*-butyl, cyclohexyl, phenyl and β -chloroethyl. When carefully purified, all of these esters polymerized with comparative ease either as pure liquids or in solution. Ultraviolet light, heat and benzoyl peroxide generally accelerated the rate of polymerization. The polymers formed by bulk polymerization were clear, hard, glassy products which were highly resistant toward scratching. These polymers have indices of refraction in the range of 1.5 to 1.6. The polymers formed in dioxane solution were precipitated by the addition of either alcohol or ether.

The polymers of the esters sometimes contained less halogen than the corresponding monomer. This may be the result of lactone formation along the chain by the loss of alkyl halide or it may have been due to loss of hydrogen halide to give unsaturation in the chain. The polymers formed slowly in solution in dioxane were generally lower in halogen than those formed rapidly by bulk polymerization under ultraviolet light.

The polymeric esters usually remained clear for long periods of time. Some samples darkened after standing for several months. In general, the polymeric bromo esters were less stable toward light than the chloro esters.

The polymeric α -bromoacrylic acid decomposed rather rapidly and gave a halogen free product. The polymer of α -chloroacrylic acid was water-

TABLE I
 ALKYL DIHALOPROPIONATES

Alkyl	Halopropionate	Yield, %	B. p. °C. at mm.	n_D^{20}	% Halogen	
					Calcd.	Found
<i>s</i> -Butyl	Dichloro ^a	88	65-66 at 25	1.4423	35.64	35.32
Cyclohexyl	Dichloro	91	95-97 at 2	1.4752	31.52	31.36
β -Chloroethyl	Dichloro	93	123-126 at 22	1.4739	51.82	48.9
<i>s</i> -Butyl	Dibromo ^b	89	130-135 at 26	1.4855	55.55	55.17
Cyclohexyl	Dibromo	93	130-132 at 2	1.5139	50.90	50.43

^a d_{20}^{20} 1.150. ^b d_{20}^{20} 1.591

soluble and on slow evaporation of the solution gave a clear film. Boiling the aqueous solution of poly- α -chloroacrylic acid produced a chlorine-free water insoluble polymer. The solubility behavior and analysis of this product indicates that it is a cross-linked poly lactone with some free hydroxyl groups.

Poly- α -chloroacrylyl chloride was also readily obtained as a white solid. It reacted readily with cold water and dissolved. This solution gave the typical clear film obtained from the corresponding acid in water solution.

Since replacement of an α -hydrogen in the polyacrylates greatly increased their hardness, it was thought of interest to try replacement of a hydrogen in the alcohol part of the molecule. A polymer of β -chloroethyl acrylate was prepared. It was not tacky as are some polyacrylates but it was not at all comparable to the isomer with halogen in the acyl part of the molecule.

Experimental

Methyl α,β -Dichloropropionate.—Five pounds (2265 g.) of technical methyl acrylate⁷ was placed in a 5-liter three-necked flask fitted with a stirrer, thermometer, inlet tube and gas trap. One liter of methanol was added and the flask was immersed in an ice-bath. Chlorine was passed into the ester rapidly over a period of five or six hours while the temperature was kept below 40°. When it seemed that no more chlorine was being absorbed the reaction was stopped. The methyl alcohol was removed by distillation into a closed system fitted with a gas trap. The flask was then fitted with a 24 in. modified column and the contents were subjected to vacuum distillation. Methyl α,β -dichloropropionate was collected distilling at 72-75° (21 mm.). The yield was 3400 g. (85%).

Methyl α,β -Dibromopropionate.—In a similar manner bromine was added to methyl acrylate to give methyl α,β -dibromopropionate, b. p. 96-98° (22 mm.) in yields of 85-88%.

α,β -Dichloropropionic Acid.—This acid has previously been prepared by a variety of methods.⁸ We have found the following procedure to be very convenient.

(7) This ester was obtained from Röhm and Haas Company, Philadelphia, Pennsylvania.

(8) Werigo and Melikoff, *Ber.*, **10**, 1499 (1877); Yarnall and Wallis, *J. Org. Chem.*, **4**, 284 (1939).

One hundred and seventy-five grams (1.11 moles) of methyl α,β -dichloropropionate and 500 cc. of 20% hydrochloric acid were gently refluxed together for five hours. The mixture was cooled, filtered through glass wool, and extracted with three 100-cc. portions of chloroform. After the solution was dried over sodium sulfate the chloroform and low-boiling products were removed by distillation under diminished pressure. The yield of crude acid remaining undistilled amounted to 105 g. (65% of the theoretical amount). Distillation of a small amount gave a product that was collected at 130-133° (26 mm.), which upon standing solidified and melted at 49-50°.

α,β -Dibromopropionic Acid.—By a similar procedure hydrolysis of methyl α,β -dibromopropionate with 48% hydrobromic acid solution gave a 72% yield of the acid, m. p. 59-60°.⁹

α,β -Dichloropropionyl Chloride.—A mixture of 105 g. of crude α,β -dichloropropionic acid and 160 g. of thionyl chloride was allowed to stand overnight and then refluxed for about an hour. On distillation 96 g. (53% of the calculated amount based on the methyl dichloropropionate used) of product boiling at 52-54° (16 mm.) was obtained.

α,β -Dibromopropionyl Chloride.—In a similar manner 400 g. of crude α,β -dibromopropionic acid and thionyl chloride gave 315 g. (77% of the calculated amount based on the methyl dibromopropionate used) of the acid chloride, b. p. 81-84° (18 mm.).¹⁰

Alkyl α,β -Dichloro- and Dibromopropionates.—The esters were prepared by adding 0.1 mole of the corresponding acid chloride to an excess of the alcohol. This mixture was heated under a reflux condenser at 100° in an oil-bath for about ten minutes and then distilled under reduced pressure. The esters and data concerning yields and properties are listed in Table I.

Phenyl α,β -Dihalopropionates.—To 0.1 mole of acid chloride in 25 cc. of dry benzene was added a solution of 9.4 g. (0.1 mole) of phenol in 25 cc. of benzene. Then 7.9 g. (0.1 mole) of pyridine was added dropwise. The mixture was shaken during the addition of pyridine and cooled so that the temperature did not go above 20°. The mixture was allowed to stand overnight at a temperature of about 5°. It was then washed with two 20-cc. portions of water to remove the pyridine hydrochloride, dried over calcium sulfate (Drierite) and distilled. The yield of phenyl α,β -dibromopropionate, b. p. 132-133° (2 mm.), was 14 g. (45.5%); n_D^{20} 1.5598.

Anal. Calcd. for $C_9H_9O_2Br_2$: Br, 51.89. Found: Br, 51.71.

(9) Münder and Tollens, *Ann.*, **167**, 226 (1873); Koheko, Koton and Florinskii, *J. Applied Chem.* (U. S. S. R.), **12**, 313 (1939).

(10) Fischer, *Ber.*, **37**, 2508 (1904).

TABLE II
ESTERS OF α -HALOACRYLIC ACIDS, $\text{CH}_2=\text{C}-\text{CO}_2\text{R}$
X

R	X	Yield, %	B. p. °C. at mm.	n_D^{20}	Element	Anal.	
						Calcd.	Found
Ethyl	Cl	81	51-53 at 18	1.4384	Cl	26.36	26.69
<i>s</i> -Butyl	Cl	58	73-73.5 at 23	1.4360	Cl	21.85	21.78
Cyclohexyl	Cl	69	51-53 at 2	1.4735	C	57.44	57.05
Phenyl	Cl	25	91-93 at 8	1.5808	H	6.91	6.85
					C	59.34	59.67
β -Chloroethyl	Cl	45	94-96 at 20	1.4729	C	35.50	35.73
					H	3.55	3.68
					Br	38.65	38.51
<i>s</i> -Butyl ^a	Br	72	80-82 at 23	1.4660	Br	34.29	34.56
Cyclohexyl	Br	54	100-106 at 4	1.4954	Br	47.53	48.08
Phenyl	Br	46	95-96 at 2	1.5480	C	47.53	48.08
					H	3.08	3.28

^a d_{20}^{20} 1.303

TABLE III
POLY- α -HALOACRYLIC ACID ESTERS $\left[\text{CH}_2-\underset{\text{X}}{\overset{\text{CO}_2\text{R}}{\text{C}}} \right]_n$

R	X	n_D^{25}	Decompn. point °C.	Elem.	Analyses, %	
					Calcd.	Found
Ethyl	Cl	1.502 \pm 0.001 ^a	160-170	Cl	26.36	23.50
<i>s</i> -Butyl	Cl	1.500 \pm .001 ^a	160-165	Cl	21.85	21.92
Cyclohexyl	Cl	1.532 \pm .001 ^b	210-235	Cl	18.81	18.46
Phenyl	Cl	1.532 \pm .001 ^b	160-168	Cl	19.43	17.72
				C	35.50	36.33
β -Chloroethyl	Cl	1.533 \pm .001 ^b	230-240	H	3.58	3.91
				Br	44.75	42.82
Ethyl	Br		125-130	Br	38.65	38.37
<i>s</i> -Butyl	Br	1.542 \pm .001 ^b	150-160	Br	34.29	34.21
Cyclohexyl	Br	1.547 \pm .001 ^b	140-150	Br	47.58	51.14
Phenyl	Br	1.612 \pm .001 ^b	175-185	C	47.58	50.92
				H	3.10	3.61

^a We are indebted to Professor T. T. Quirke of the Department of Geology, University of Illinois for these values.

^b We are indebted to Dr. R. S. Rowland of the Illinois State Geological Survey for these values.

The yield of phenyl α,β -dichloropropionate, b. p. 130-135° (18 mm.) was 41%; n_D^{20} 1.5262.

Anal. Calcd. for $\text{C}_9\text{H}_8\text{O}_2\text{Cl}_2$: Cl, 32.38. Found: Cl, 32.16.

Alkyl and Phenyl α -Haloacrylates.—The α -haloacrylates were prepared by heating together about 0.07 mole of the dihaloester and 0.10 mole of quinoline, quinaldine or dimethylaniline at 100° for ten minutes in a nitrogen atmosphere. The mixture was then distilled under reduced pressure. The distillate was dissolved in about three volumes of chloroform and this solution was washed thoroughly with 5% hydrochloric or sulfuric acid to remove any amine. The chloroform solution was then dried over anhydrous sodium sulfate and distilled. The data on yields, physical properties and analyses are collected in Table II.

Polymers of the α -Haloacrylic Ester.—The α -haloesters were polymerized in various manners such as standing at room temperature for about two to three weeks; heating to 100° for twenty to thirty minutes; adding a trace of benzoyl peroxide and allowing to stand at room temperature or heating slightly; exposure to ultraviolet light at room temperature for six to eight hours; solution in dioxane, addition of a trace of benzoyl peroxide and standing

for two days; etc. In bulk polymerization experiments, clear, hard, glassy products were obtained. The polymers prepared in dioxane solution were precipitated with either ether or alcohol as white powders. Unless the esters were carefully purified, polymerization was very slow. In Table III the properties of the polymers are described.

α -Chloroacrylic Acid.¹¹—To a mixture of 275 g. of barium hydroxide octahydrate and 500 cc. of water in a 1-liter two-necked flask equipped with a stirrer and dropping funnel was added dropwise 110 g. of methyl α,β -dichloropropionate. After stirring for two hours the mixture was acidified with a solution of 62.5 g. of concentrated sulfuric acid in 125 cc. of water. The acidified mixture was extracted with five 200-cc. portions of ether containing a total of 1 g. of hydroquinone. The ether extract was dried over anhydrous magnesium sulfate and the ether was evaporated under diminished pressure at room temperature. The solid residue was recrystallized from low-boiling petroleum ether to give 46 g. (62%) of α -chloroacrylic acid, m. p. 64-65°.

α -Bromoacrylic Acid.—A similar hydrolysis of methyl α,β -dibromopropionate gave a 70% yield of α -bromo-

(11) This procedure was adapted from that of Werigo and Werner, *Ann.*, **170**, 168 (1873).

acrylic acid, m. p. 71–72° (from low-boiling petroleum ether).¹²

Poly- α -chloroacrylic Acid.—A solution of 75 g. of α -chloroacrylic acid in 500 cc. of anhydrous alcohol-free ether was allowed to stand under a mercury vapor lamp for three days. A considerable amount of solid separated from solution during this period. The ether was poured off, the flask broken and the polymer chipped away from the glass. The yield was 55 g.

Anal. Calcd. for $C_3H_3O_2Cl$: Cl, 33.3. Found: Cl, 32.6.

In another experiment 10 g. of α -chloroacrylic acid was melted in a water-bath held at 70° and 0.1 g. of powdered benzoyl peroxide was added. The liquid became cloudy almost at once and the polymerization seemed to be complete in fifteen minutes. The light yellow solid was pulverized and washed with ether. The yield was 5.5 g. The polymeric material melted at about 300°. It was soluble in cold water and on evaporation of a water solution at low temperatures, clear, tough, colorless films were formed.

When a solution of 10 g. of the polymer in 50 cc. of water was heated to boiling, a gel formed which filled the vessel in which the mixture was boiling. This gel then hardened to an easily pulverizable mass which had little coherence. On drying it became powdery. It did not contain halogen and apparently is a cross-linked lactone with some hydroxyl groups. It dissolved when boiled with alkali.

Anal. Calcd. for $C_3H_2O_2$: C, 51.4; H, 2.8. Found: C, 47.76, 45.45; H, 4.00, 3.77. These analyses were made on different samples.

α -Chloroacrylyl Chloride.—In a 100-cc. modified Claisen flask fitted with an efficient condenser was placed 25 g. of freshly distilled diethylaniline. An oil-bath about the distilling bulb was heated to 85° and the system was placed under a vacuum of 70–80 mm. From a dropping funnel reaching almost to the bottom of the distilling flask was introduced slowly 25 g. of α,β -dichloropropionyl chloride. During the distillation the receiver was kept in an ice-salt-bath. About 12 g. of liquid was collected which was redistilled and the fraction boiling at 45–48° (78–80 mm.) was collected as α -chloroacrylyl chloride; yield, 7.2 g. or 37% of theory; n_D^{20} 1.4689.

Anal. Calcd. for $C_3H_2OCl_2$: Cl, 56.7. Found: Cl, 55.4.

Poly- α -chloroacrylyl Chloride.—In a quartz test-tube was placed a solution of 8 g. of α -chloroacrylyl chloride in 10 cc. of dry carbon tetrachloride. The test-tube was

stoppered tightly with a tinfoil covered stopper and placed under a mercury vapor lamp for three days. The white solid was removed by filtration and washed with dry carbon tetrachloride; m. p. 210–225°; yield, 5.4 g. or 67% of the theory.

Anal. Calcd. for $C_3H_2OCl_2$: Cl, 56.7. Found: Cl, 53.2.

Two grams of α -chloroacrylyl chloride was placed in a small thin-walled test-tube. The tightly stoppered test-tube was placed under an ultraviolet lamp for three days. By this time the liquid had changed to a clear, tan, brittle solid.

One gram of poly- α -chloroacrylyl chloride was dissolved in 10 cc. of water by shaking for about ten minutes. The water was evaporated leaving a clear film very similar to the film obtained directly from poly- α -chloroacrylic acid.

Poly- α -bromoacrylic Acid.—This polymer was obtained from α -bromoacrylic acid by the method used for the chloro compound. It was relatively unstable and lost hydrogen bromide rapidly at room temperature.

Anal. Calcd. for $C_3H_3O_2Br$: Br, 53.0. Found: Br, 51.3.

Poly- β -chloroethyl Acrylate.—Fifty grams of β -chloropropionyl chloride was added slowly with cooling and stirring to 35 g. of ethylene chlorohydrin. The reaction mixture was allowed to stand for two hours and then distilled. The yield of β -chloroethyl β -chloropropionate was 62 g. (92%), b. p. 109–111° (20 mm.), n_D^{20} 1.4600.

Anal. Calcd. for $C_6H_8O_2Cl_2$: Cl, 41.5. Found: Cl, 41.04.

Treatment of 60 g. of the above ester with 50 g. of quinoline at 150–160° for twenty minutes followed by isolation of the ester in the usual way gave 25 g. (53%) of β -chloroethyl acrylate; b. p. 64–66° (20 mm.), n_D^{20} 1.4490.

Anal. Calcd. for $C_6H_7O_2Cl$: C, 44.77; H, 5.22. Found: C, 44.54; H, 5.33.

Two grams of this ester was placed in a sample tube under the mercury vapor lamp. In three days the ester had changed to a soft, rubbery, water-clear material. Longer exposure did not cause the polymer to become harder.

Anal. Calcd. for $C_6H_7O_2Cl$: C, 44.77; H, 5.22. Found: C, 44.94; H, 5.26.

Summary

A series of esters of α -chloroacrylic acid and α -bromoacrylic acid have been prepared and polymerized to give hard, white polymers with rather high refractive indices.

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(12) This acid has been described by Lossen and Kouski, *Ann.*, **342**, 135 (1905).