placed next to the flask as a source of illumination. The reaction proceeded rapidly at room temperature. After the addition was complete, the reaction mixture was washed with sodium bisulfite followed by water, dried and rectified to give principally the tetrabromo addition product along with some of the dibromo compound.

Bromination of 2,7-Dimethyl-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene.—This olefin was brominated in a similar manner with the exception that the reaction temperature was maintained at the reflux temperature of the mixture. Only the tetrabromo addition product was isolated.

Bromination of 5,5,6,6,7,7,7-Heptafluoro-3-heptene.—A solution of 150 g. of the olefin in 100 ml. of carbon tetrachloride was cooled to 12° and a solution of 120 g. of bromine in 100 ml. of carbon tetrachloride was added dropwise. The reaction was illuminated by a 150-watt light bulb placed next to the flask. After one-half the bromine was added, the temperature rose to 22° and hydrogen bromide was liberated. The temperature was lowered to 10° and the remaining bromine added. After standing for 12 hours at room temperature, the reaction mixture was refluxed for two hours causing further liberation of hydrogen bromide. The solution was then washed with sodium bicarbonate followed by water, dried and rectified. Both the dibromo addition product and an olefin resulting from its dehydrobromination were obtained. The latter material was not identified.

Bromination of 2-Methyl-4,4,5,5,6,6,6-heptafluoro-2-hexene.—A solution of 160 g. of the olefin in 150 ml. of chloroform was placed in the flask and a mixture of 125 g. of bromine in 100 ml. of chloroform was added dropwise. No cooling was employed and the reaction temperature rose rapidly to reflux with the liberation of hydrogen bromide. After the addition was complete, the mixture was refluxed for 48 hours. The solution was then washed with sodium bicarbonate followed by water, dried and rectified. The dibromo addition product was obtained as well as two bromine substituted derivatives of the starting material.

Acknowledgment.—The authors wish to express their appreciation to the Petroleum Branch, Materials Laboratory, Wright Air Development Center, Dayton, Ohio, for supporting this work.

Lafayette, Ind.

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

The Structure of the Polymers of α-Haloacrylates

By C. S. Marvel, E. D. Weil, L. B. Wakefield and C. W. Fairbanks

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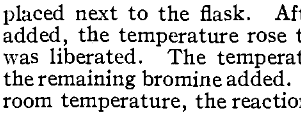
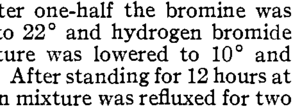
The present investigation shows that the earlier assignment of a "head-to-head" arrangement of the monomer units in polyalkyl α-haloacrylates was based on a misinterpretation of the reactions of these polymers. These polymers have been proved to have predominantly the "head-to-tail" structure.

Experimental results obtained in this Laboratory have previously been presented[1] as evidence that the polymers of α-haloacrylic esters have a "head-to-head" arrangement of monomer units I rather than the usual "head-to-tail" structure II.



$$\left[-\mathrm{CH_2}-\underset{\mathrm{CO_2R}}{\overset{\mathrm{X}}{\mathrm{C}}}-\underset{\mathrm{CO_2R}}{\overset{\mathrm{X}}{\mathrm{C}}}-\mathrm{CH_2}-\right]_x$$

I



$$\left[-\mathrm{CH_2}-\underset{\mathrm{CO_2R}}{\overset{\mathrm{X}}{\mathrm{C}}}-\mathrm{CH_2}-\underset{\mathrm{CO_2R}}{\overset{\mathrm{X}}{\mathrm{C}}}-\right]_x$$

II

X = Cl or Br, R = alkyl

Since all other vinyl homopolymers investigated to date have been shown to have predominantly a "head-to-tail" structure, further study of this apparent anomaly has been undertaken.

The evidence originally presented as indicative of the head-to-head structure of polymethyl α-bromoacrylate may be summarized as follows: 1. Treatment of the polymer with an alkali iodide in acetone or aqueous dioxane results in the liberation of approximately as much iodine as is produced in the reaction of an alkali iodide with diethyl α,β-dibromosuccinate under similar conditions. 2. The polymer loses hydrogen bromide at a lower temperature than is required to dehydrobrominate diethyl α,γ-dibromo-α,γ-diethylglutarate. 3. The product made by treating the polymer with aqueous alkali slowly reduces periodic acid. 4. Treatment of the polymer with zinc in refluxing dioxane removed 97% of the bromine, 11% more than the statistical calculations of Flory[2] indicate could be removed from structure II by formation of cyclopropane rings.

The present investigation shows that this evidence does not justify the assignment of structure I to the α-haloacrylate polymers, and evidence for structure II has been obtained.

Further study of the action of alkali iodides on polymethyl α-bromoacrylate indicates that the reaction is more complex than was originally believed. The product obtained by treating the polymer with potassium iodide in wet dioxane at 100° is a dark red tar, largely water-soluble, resembling the product obtained from the dehydrobromination of the polymer by heating with quinoline. Treatment of polymethyl α-bromoacrylate with sodium iodide in refluxing acetone yields a tan powder which has infrared bands at 1786 cm.$^{-1}$ (lactone carbonyl), 1736 cm.$^{-1}$ (unconjugated ester carbonyl) and only a trace of absorption indicative of carbon-to-carbon double bonds.[3] Polymethyl α-bromoacrylate when allowed to stand at room temperature for three weeks in a solution of sodium iodide in methyl cellosolve–dioxane mixture liberated iodine equivalent to 90% completion of the hypothetical 1,2-elimination of halogen. The product however showed strong infrared bands at 1777 cm.$^{-1}$ (γ-lactone carbonyl), 1730 cm.$^{-1}$ (conjugated ester carbonyl), and a weak band at 1625 cm.$^{-1}$ indicative of olefinic linkages. The interpretation of the reaction of alkali iodides with polymethyl α-bromoacrylate as a 1,2-elimination of halogen from structure I is placed in considerable doubt by this evidence.

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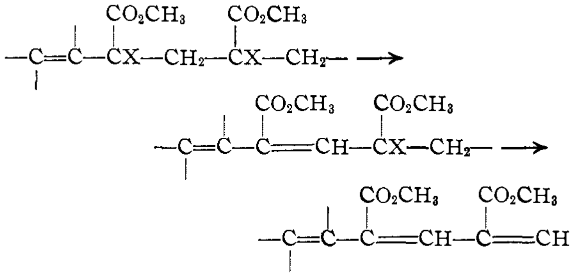
(1) C. S. Marvel and J. C. Cowan, This Journal, **61**, 3156 (1939).

(2) P. J. Flory, *ibid.*, **61**, 1518 (1939); *cf.* F. T. Wall, *ibid.*, **62**, 803 (1940).

(3) The infrared spectra discussed in this article were obtained on samples in Nujol mull, unless otherwise specified. The authors are indebted to Mrs. Elizabeth Petersen Leighly and Miss Helen Miklas, who obtained the spectra and assisted in their interpretation.

The facile thermal dehydrobromination of polymethyl α-bromoacrylate has already been noted. This behavior would be expected of polymers having structure II[4]; the existence of a single olefinic bond per chain is theoretically sufficient to start a process of allylic activation and dehydrohalogenation of the polymer chain.

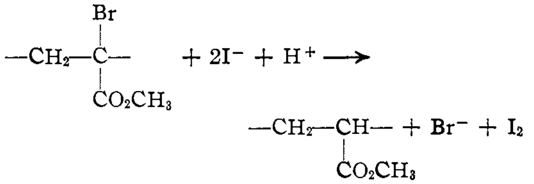


$$-\underset{|}{C}=\overset{|}{C}-\overset{CO_2CH_3}{\overset{|}{C}X}-CH_2-\overset{CO_2CH_3}{\overset{|}{C}X}-CH_2-\longrightarrow$$

$$-\underset{|}{C}=\overset{|}{C}-\overset{CO_2CH_3}{\overset{|}{C}}=CH-\overset{CO_2CH_3}{\overset{|}{C}X}-CH_2-\longrightarrow$$

$$-\underset{|}{C}=\overset{|}{C}-\overset{CO_2CH_3}{\overset{|}{C}}=CH-\overset{CO_2CH_3}{\overset{|}{C}}=CH-$$

The replacement of the bromine by iodine in polymethyl α-bromoacrylate would very probably increase the ease of dehydrohalogenation of the polymer.[5] Consequently, reactions such as (1) may account for the liberation of iodine on treatment of polymethyl α-bromoacrylate with an iodide. In addition to the mineral acid itself, carboxyl groups engendered in the polymer by the action of hydrogen halide on ester linkages may supply the protons required by the stoichiometry of reaction (1).



$$-CH_2-\overset{Br}{\underset{CO_2CH_3}{C}}- + 2I^- + H^+ \longrightarrow -CH_2-\underset{CO_2CH_3}{CH}- + Br^- + I_2 \quad (1)$$

meso-α,γ-Dibromoglutaric acid on standing at room temperature for four weeks with excess potassium iodide in wet dioxane under nitrogen liberated 0.8 mole of iodine per mole of acid. The corresponding dimethyl ester liberated only a trace of iodine under the same conditions, but yielded dimethyl α,γ-diiodoglutarate, which could be made to liberate 0.53 mole of iodine per mole of ester on refluxing for 72 hours with excess potassium iodide in 10:1 dioxane-water mixture, under which conditions the medium became acidic through hydrolysis of the ester.

The reaction of alkali iodides with polymethyl α-bromoacrylate is further complicated by extensive lactonization of the polymer during the reaction and in the subsequent isolation procedure. Although the chemistry of the iodide reaction is not as yet fully clarified, the reaction appears to be of doubtful value in differentiating between structures I and II of the polymer.

In the original study[1] of polymethyl α-bromoacrylate, the brown substance obtained by treatment of the polymer with hot concentrated aqueous alkali was found to reduce periodic acid slowly, the amount of reduction varying from sample to sample. Polymers hydrolyzed in this manner undoubtedly have undergone some dehydrohalogenation. Therefore, the reaction with periodic acid was reinvestigated using the nearly-colorless halogen-free product obtained by treatment of polymethyl α-bromoacrylate with moist silver oxide. The rate at which this substance reduced periodic acid was found to be comparable to the rate of reduction by an α-hydroxy acid (Table I).

TABLE I

Reductant	Meq. of periodic acid reduced per millimole[a] of sample 30 min.	10 hr.	174 hr.
(1) DL-Dimethyltartaric acid	2.1	...	...
(2) α-Hydroxyisobutyric acid	0.0	0.3	3.6
(3) Polymethyl α-bromoacrylate hydrolyzed by silver oxide	0.0	0.0	1.4

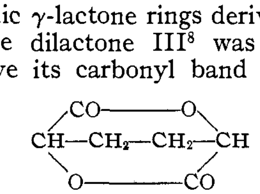
[a] Millimolecular weight of the unit $-CH_2C(OH)(CO_2CH_3)-$ was used for (3).

The conclusion that the reduction of periodic acid by the polymeric hydrolysis product indicates a head-to-head structure is clearly not justified.

Polymethyl α-bromoacrylate can be completely debrominated by refluxing with zinc dust in dioxane, whereas statistical calculations show that a polymer chain with halogen atoms on alternate carbon atoms could lose only 86.47% of its halogen by formation of cyclopropane rings. These calculations are based on the assumption that no other halogen-removing reaction occurs, and are therefore inapplicable to the present case, since the infrared absorption spectrum of the debrominated polymer shows a strong band at 1794 cm.$^{-1}$ indicative of lactone carbonyl groups, which are engendered by a halogen-removing reaction.

The corresponding chlorine-containing polymer lost only 16% of its chlorine in one week of refluxing in dioxane with zinc dust, and the product had an absorption band at 1021 cm.$^{-1}$ indicative of cyclopropane rings,[6] which suggests that polymethyl α-chloroacrylate has structure II.

Polymethyl α-bromoacrylate undergoes partial lactonization under conditions similar to those used by Minsk and Kenyon[7] for lactonization of poly-α-chloroacrylic acid; polymethyl α-chloroacrylate requires much longer treatment. Both polylactones show a strong infrared absorption band at 1794 cm.$^{-1}$ in Nujol mull or 1795 cm.$^{-1}$ in dioxane. These bands are intermediate in wave number between those of carbonyl groups in four- and five-membered lactone rings. Such an absorption band might be explained by postulating bicyclic δ-lactone rings derived from structure I, or spiro- and/or bicyclic γ-lactone rings derived from structure II. The dilactone III[8] was prepared and found to have its carbonyl band at 1784 cm.$^{-1}$



III

in Nujol mull and 1788 cm.$^{-1}$ in chloroform. A model compound for the polylactone derivable from structure II was prepared by the following ser-

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[4] C. C. Price, "Mechanisms of Reactions at Carbon-Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 73.

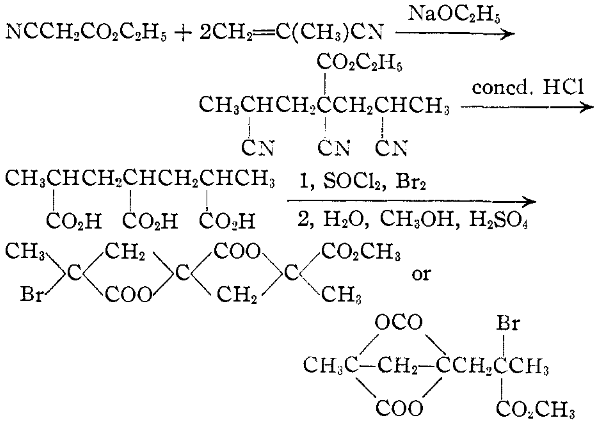
[5] E. D. Hughes, *Quart. Revs.*, **5**, 263 (1951).

[6] J. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL, **71**, 2482 (1949).

[7] L. M. Minsk and W. O. Kenyon, *ibid.*, **72**, 2650 (1950).

[8] H. R. LeSueur, *J. Chem. Soc.*, **93**, 720 (1908).

ies of reactions, in which the final step was carried out under conditions similar to those used in lactonization of the polymer.



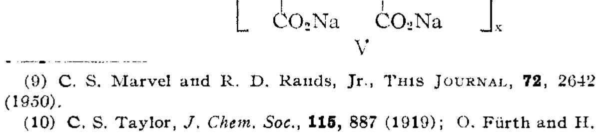
IV

The substance IV, probably a mixture of isomeric dilactones, has a sharp carbonyl band at 1794 cm.$^{-1}$ (in chloroform) as well as a normal ester band at 1737 cm.$^{-1}$. These results favor structure II for the original polymer, but the closeness of the values for the lactone carbonyl bands of III and IV prevents a definite conclusion based on this evidence.

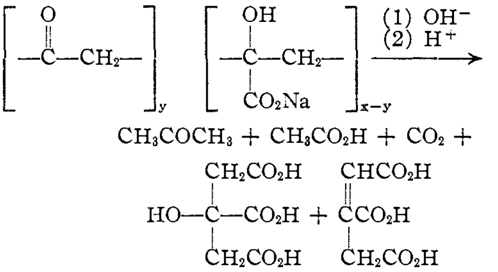
Polymethyl α-bromoacrylate dissolves in alkali only with difficulty, giving a dark red solution from which it tends to precipitate on boiling. The polylactone, however, dissolves readily in tenth normal sodium hydroxide at room temperature to give a pale orange solution, and was therefore employed in oxidative degradation experiments instead of the unlactonized polymer.

The saponified polylactone when boiled with hydrogen peroxide in strongly alkaline solution undergoes concurrent oxidation and cleavage to yield acetone, acetic acid, carbon dioxide, formic acid and a mixture of solid acids of which aconitic acid is the main component together with traces of citric and citraconic or itaconic acids. The maximum yields of acetone and acetic acid were obtained in a single experiment, being 88 and 360 mg., respectively, from 2.0 g. of the polylactone. The solid acids were identified by their positions on a partition chromatogram using the method of Marvel and Rands[9] and by color tests[10] on the separated acids; aconitic acid was isolated and characterized by comparison of its infrared spectrum with that of an authentic specimen.

These products are satisfactorily explained only on the basis of a primarily head-to-tail structure II of polymethyl α-bromoacrylate and of its saponification product V. The main reactions involved in the degradation procedure are



V



The head-to-head structure I would be expected to yield some succinic acid on oxidative degradation, and a minor fraction of such structural units in polymethyl α-bromoacrylate is not excluded by this work. A trace of acid was eluted from the chromatograph at the characteristic peak effluent volume[9] of succinic acid. However, no succinic acid could be isolated from the eluate and only a gummy residue was obtained which gave a brown color with the acetic anhydride–pyridine reagent.[10] Succinic acid gives no color with this reagent.

Experimental[11]

Polymethyl α-Bromoacrylate.[1]—To 75 ml. of a 2% aqueous solution of MP-635-S emulsifier[12] were added 40 g. of freshly redistilled methyl α-bromoacrylate[1] (b.p. 37.0–37.5° at 5.5 mm.), 1 ml. of 7.3% ammonium persulfate solution and 1 ml. of 3.7% sodium metabisulfite solution. The container was sealed and agitated at 30° for ten hours. The emulsion was coagulated by pouring it into dilute alum solution with stirring. The coagulum was then dissolved in dioxane, filtered and reprecipitated in water, giving a 95% yield of brittle white polymer having an inherent viscosity of 0.4 in dioxane.

Anal. Calcd. for $(C_4H_5O_2Br)_x$: Br, 48.44. Found: Br, 46.56.

Polymethyl α-bromoacrylate was also prepared in dioxane solution with the use of benzoyl peroxide as the initiator, and the product was found to have chemical properties and an infrared spectra identical to those of the polymer produced in emulsion. The yields, however, were only 50–65%, and the inherent viscosity was 0.2.

Polyethyl α-Chloroacrylate.—Ethyl α-chloroacrylate[13] was polymerized in emulsion as described above, giving an 88% yield of white polymer having an inherent viscosity of 2.53. X-Ray diffraction patterns on cold-drawn films prepared from this polymer were diffuse, as expected in view of the presence of an asymmetric carbon atom in the monomer unit.

Polymethyl α-Chloroacrylate.—Methyl α-chloroacrylate[13] was polymerized in dioxane using benzoyl peroxide as the initiator; a white brittle polymer of inherent viscosity 0.11 was obtained in 50% yield.

Reaction of Potassium Iodide with Polymethyl α-Bromoacrylate in Wet Dioxane.—In 40 ml. of purified dioxane was dissolved 0.4219 g. of polymethyl α-bromoacrylate. Two grams of potassium iodide was added and dissolved by the admixture of the minimum amount of water, and the solution was heated on the steam-bath for 72 hours. The liberated iodine was then titrated with sodium thiosulfate, requiring 2.226 milliequivalents.

The experiment was repeated and an attempt made to isolate the product. The dioxane was evaporated leaving a black tar which was extracted with water to remove the potassium salts. However, practically all of the tar went into solution or emulsion, and extraction with organic sol-

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[9] C. S. Marvel and R. D. Rands, Jr., THIS JOURNAL, **72**, 2642 (1950).

[10] C. S. Taylor, *J. Chem. Soc.*, **115**, 887 (1919); O. Fürth and H. Herrmann, *Biochem. Z.*, **280**, 448 (1935).

[11] The analyses reported herein were performed by Miss Emily Davis, Miss Jean Fortney, and Mrs. Katherine Pih of the University of Illinois Microanalytical Laboratory, and by the Clark Microanalytical Laboratory, Urbana, Illinois.

[12] A sodium alkane sulfonate emulsifier, for which we are indebted to Dr. Stanley Detrick of the Jackson Laboratory of E. I. du Pont de Nemours and Company.

[13] C. S. Marvel, J. Dec, H. G. Cooke, Jr., and J. C. Cowan, THIS JOURNAL, **62**, 3496 (1940).

vents failed. The polymer emulsion remained dark even on prolonged treatment with excess sodium thiosulfate.

Reaction of Sodium Iodide with Polymethyl α-Bromoacrylate in Acetone.—Ten grams of polymethyl α-bromoacrylate was refluxed for 24 hours with 45 g. of sodium iodide in 350 ml. of pure acetone. The solvent was removed by evaporation and the tarry residue was reprecipitated several times from acetone by addition of water. The light tan polymer thus isolated reduced permanganate and had infrared bands at 1736 cm.$^{-1}$ (normal ester carbonyl) and 1786 cm.$^{-1}$ (strained lactone carbonyl) but only a trace of absorption in the carbon–carbon double bond region.

Reaction of Sodium Iodide with Polymethyl α-Bromoacrylate in Methyl Cellosolve–Dioxane Mixture.—A solution of 8.25 g. of polymethyl α-bromoacrylate in 75 ml. of pure dioxane was added to a solution of 150 g. of sodium iodide in 400 ml. of methyl cellosolve, causing precipitation of part of the salt. After the mixture had stood for three weeks at room temperature, titration of an aliquot with sodium thiosulfate indicated the presence of iodine equivalent to 90% completion of the hypothetical 1,2-dehalogenation of structure I. Addition of the remainder of the solution to water caused precipitation of the polymer, which was separated by centrifugation, washed successively with water, methanol, and ether, dissolved in dioxane, then reprecipitated by the addition of methanol, and collected on a filter.

Reaction of Potassium Iodide with *meso*-α,γ-Dibromoglutaric Acid.—Twenty-five grams of potassium iodide was dissolved in 300 ml. of dioxane containing enough water to effect the dissolution of the iodide. To this was added 10.00 g. of *meso*-α,γ-dibromoglutaric acid,[14] and the mixture was sealed under nitrogen. After four weeks at room temperature, the liberated iodine was determined by titration of an aliquot with thiosulfate; a total of 55.5 meq. of iodine was present.

Reaction of Potassium Iodide with Dimethyl *meso*-α,γ-Dibromoglutarate.—The procedure was identical to that used with the acid, employing 25 g. of dimethyl *meso*-α,γ-dibromoglutarate[14] in 250 ml. of dioxane. After a week at room temperature, only 0.87 meq. of iodide was present. The dioxane was removed under reduced pressure, the residue was taken up with water and ether, and the layers were separated. The ether layer upon evaporation yielded a mixture of crystals and an oil. The crystals, after recrystallization from methanol, melted at 72.5–73.5°, the reported m.p. for dimethyl *meso*-α,γ-diiodoglutarate,[14] and were shown by sodium fusion to contain iodine but no bromine.

Reaction of Potassium Iodide with Dimethyl *meso*-α,γ-Diiodoglutarate.—In 10 ml. of dioxane was dissolved 112 mg. of dimethyl *meso*-α,γ-diiodoglutarate; a solution of 0.40 g. of potassium iodide in 1.0 ml. of water was added, and the mixture was refluxed for three days. Titration with thiosulfate showed that 0.29 meq. of iodine had been liberated.

Reaction of Polymethyl α-Bromoacrylate with Zinc.—Five grams of zinc dust (activated by washing successively with dilute hydrochloric acid, water and acetone) and 1.5 g. of polymethyl α-bromoacrylate were refluxed vigorously in three liters of pure dioxane for one week. The dioxane was evaporated under reduced pressure until the volume was 50 ml. The solution was filtered, added to water, the precipitated polymer removed by filtration, dissolved in dioxane, and reprecipitated by addition to ether. A low yield of yellow polymeric material was obtained. The product gave a negative sodium fusion test for halogen. Infrared curves showed carbonyl peaks at 1742 cm.$^{-1}$ (nonconjugated ester) and 1792 cm.$^{-1}$ (lactone carbonyl).

Reaction of Polymethyl α-Chloroacrylate with Zinc.—The same procedure was employed as was used in the zinc treatment of polymethyl α-bromoacrylate. The product was a very pale yellow polymer which was found to contain 25.20% chlorine; a loss of 16% of the original chlorine had occurred. An infrared curve showed a strong band at 1021 cm.$^{-1}$ (cyclopropane ring) in Nujol mull. An infrared curve run for comparison on *cis*-1,2-dicarbethoxycyclopropane[15] showed a band at 1027–1035 cm.$^{-1}$ (as the pure liquid).

Lactonization of Polymethyl α-Bromoacrylate.—To a solution of 20 g. of polymethyl α-bromoacrylate in 200 ml. of pure dioxane were added 100 ml. of methanol, 25 ml. of water and 5 ml. of concentrated sulfuric acid. The mixture was refluxed for two days, then poured into water. The precipitated polylactone was collected on a filter, washed with water, and dried. Its infrared spectrum showed a normal ester carbonyl band at 1735 cm.$^{-1}$ and a strong band at 1794 cm.$^{-1}$ attributable to a lactone carbonyl group.

Lactonization of Polymethyl α-Chloroacrylate.—Polymethyl α-chloroacrylate was treated according to the procedure above; however, the polymer gelled during the refluxing. The gel was dried and powdered; its infrared spectrum showed a lactone band at 1794 cm.$^{-1}$.

2,4,6-Tricyano-4-carbethoxyheptane.—To a solution of 4.5 g. of sodium in 100 ml. of absolute ethanol was added 57 g. of ethyl cyanoacetate and 67 g. of methacrylonitrile (Shell Development; redistilled, b.p. 87–89.5°) was then added dropwise with mechanical stirring over the course of an hour. The reaction was initiated by warming to 35° for about 1.5 hours. The mixture was warmed briefly to a temperature of 45°, then cooled, poured into water, neutralized with dilute hydrochloric acid, and extracted with ether. The ether was evaporated leaving about 50 ml. of viscous liquid which partially crystallized on standing. The material was fractionally distilled under diminished pressure and the fraction boiling at 193.5–197° (2.5 mm.) and weighing 36.5 g., was taken as representing the bis-condensation product. The distillate crystallized and was recrystallized from ether–cyclohexane mixture, yielding 20 g. of colorless prisms, m.p. 54–55° (uncor.), soluble in alcohol, benzene and warm ether, insoluble in cyclohexane; this substance may be a mixture of several optical isomers.

Anal. Calcd. for $C_{13}H_{17}O_2N_3$: C, 63.14; H, 6.93; N, 16.99. Found: C, 63.04; H, 7.06; N, 17.01.

An experiment in which benzyltrimethylammonium hydroxide (Triton B) was used as catalyst for this reaction was entirely unsuccessful.

Heptane-2,4,6-tricarboxylic Acid.—Twenty grams of 2,4,6-tricyano-4-carbethoxyheptane was refluxed for two days with 80 ml. of concentrated hydrochloric acid; the excess acid was allowed to evaporate under reduced pressure and the residue exhaustively extracted with ether. The combined extracts were allowed to evaporate, leaving a gum which crystallized on standing. The product was recrystallized several times from ether and from benzene–acetone mixture, yielding 10 g. (54%) of small colorless prisms, m.p. 151–152° (uncor.).

Anal. Calcd. for $C_{10}H_{16}O_6$: C, 51.70; H, 6.94. Found: C, 51.53; H, 7.14.

Dilactone Derivative of 2,4,6-Tribromo-2,4,6-tricarbomethoxyheptane.—Two grams of heptane-2,4,6-tricarboxylic acid was warmed at 50° for ten hours with 10 ml. of thionyl chloride, and the excess of the latter taken off under reduced pressure. Ten milliliters of dry bromine was added in portions over the course of 12 hours at 50–60°. Twenty milliliters of water was added, and the solid which settled out after reaction ceased was collected by filtration. After recrystallization from an acetone–chloroform mixture, the product was colorless, microcrystalline, and decomposed gradually above 170°; the yield was 2 g. Analysis showed the product to be partially lactonized. The lactonization was completed by refluxing for six hours with 10 ml. of 10:1 methanol–water mixture containing two drops of concentrated sulfuric acid. The product, after recrystallization from a benzene–acetone mixture, consisted of small colorless needles, m.p. 175–177° (with decomposition) and was insoluble in water, cold methanol and dilute sodium bicarbonate solution.

Its infrared spectrum showed a strong ester carbonyl peak at 1737 cm.$^{-1}$ (in chloroform) and a strong lactone carbonyl peak at 1794 cm.$^{-1}$ as well as a weak carbonyl peak at 1712 cm.$^{-1}$ (evidently a carboxylic impurity).

Anal. Calcd. for $C_{11}H_{13}O_6Br$: C, 41.14; H, 4.08; Br, 24.88. Found: C, 40.88; H, 4.55; Br, 24.64.

Hydrolysis of Polymethyl α-Bromoacrylate.—Thirty grams of polymethyl α-bromoacrylate was dissolved in 500 ml. of tetrahydrofuran, and moist silver oxide, freshly prepared from 400 g. of silver nitrate, was added. The mixture was refluxed for two days, carefully protected from light by a tinfoil cover, then filtered into excess ether. The resulting white polymeric precipitate was collected by filtration.

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[14] C. K. Ingold, *J. Chem. Soc.*, **119**, 316 (1921).

[15] F. Fichter and H. Spiegelberg, *Helv. Chim. Acta*, **12**, 1162 (1929).

Oxidation of Hydrolyzed Polymethyl α-Bromoacrylate, DL-Dimethyltartaric Acid[16] and α-Hydroxyisobutyric Acid.—Approximately 1 meq. of each substance (molecular weight divided by number of carboxyl or carbomethoxy groups in the molecule) was dissolved in 10.0 ml. of 1.5% sodium hydroxide, 100.0 ml. of 0.5% periodic acid solution was added, and the flask was allowed to stand at room temperature. At intervals, one-tenth aliquots were removed, added to excess potassium iodide solution and the iodine quickly titrated with 0.0990 *N* thiosulfate. The results are given in Table I.

Oxidation and Alkaline Cleavage of Saponified Polymethyl α-Bromoacrylate Polylactone.—The polylactone and the product of silver oxide hydrolysis of polymethyl α-bromoacrylate were resistant to degradation by nitric acid, and gave no identifiable products upon treatment with lead tetraacetate or periodic acid. However, the alkaline oxidation methods tried, using permanganate, periodate or hydrogen peroxide, invariably gave some acetone and acetic acid. The best yields of identifiable degradation products were obtained by the procedure below.

Two grams of polymethyl α-bromoacrylate polylactone was weighed into a flask and dissolved in the minimum amount of 5% sodium hydroxide at room temperature. The yellow solution was saturated with carbon dioxide, 30 ml. of 30% hydrogen peroxide was added, and the mixture was warmed gently until the color was discharged and gas evolution began. After one-half hour, 25 ml. of 20% sodium hydroxide was added, and the solution was steam distilled slowly into a chilled receiver containing a saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. Acetone codistilled with the steam over the course of several hours, during which time five additional 10-ml. portions of hydrogen peroxide and 20 ml. more of 20% sodium hydroxide were added. The precipitate in the receiver was collected on a weighed filter paper and dried to constant weight, yielding 369 mg. of acetone 2,4-dinitrophenylhydrazone, m.p. 122–123° crude, 124–125° recrystallized. The compound did not depress the melting point of an authentic sample of acetone 2,4-dinitrophenylhydrazone.

Anal. Calcd. for $C_9H_{10}N_4O_4$: C, 45.39; H, 4.23; N, 23.53. Found: C, 45.17; H, 4.20; N, 23.59.

The residual liquid in the distilling flask was acidified to congo red with 6 *N* sulfuric acid, resulting in vigorous evolution of carbon dioxide, and then distilled until only a sludge of crystals and sirup remained. The total acid content of the distillate was found by titration of an aliquot to be 6.7 meq. The silver nitrate test indicated only a trace of halide. The formic acid content as determined by the mercuric chloride method[17] on an aliquot was 0.74 meq.; consequently the distillate contained 6.0 meq. of acetic acid which was characterized as its *p*-bromophenacyl ester, observed m.p. 84–85°, and *p*-nitrobenzyl ester, observed m.p. 77°. Neither of these derivatives depressed the melting points of authentic samples.

Exhaustive ether extraction of the residual material in the distilling flask and evaporation of the ether yielded a gummy mixture of water-soluble acids which was subjected to partition chromatography by the method of Marvel and Rands,[9] using 0.4 *N* sulfuric acid on 100-mesh silicic acid as the fixed phase and chloroform–butanol mixtures of increasing polarity as the eluant. The "chromatogram" (plot of volume of standard alkali needed to titrate each portion of effluent against total volume of effluent) revealed peaks at the characteristic peak effluent volumes of acetic, itaconic (and/or citraconic), aconitic and citric acids. The presence of citric and aconitic acids was substantiated by characteristic color reactions on the residues obtained by evaporating the proper eluant portions. A chromatograph on a tenfold scale yielded sufficient aconitic acid for positive identification. Aconitic acid crystallized from the eluant, upon concentration, as the free acid, m.p. 175–180° crude (with decomposition), and was characterized by comparison of the infrared spectrum with that of an authentic sample. The presence of either itaconic or citraconic acid or both was indicated by color tests as in the case of citric acid, but the amount isolated from the eluate was too small to permit more definite identification. A trace of acid was eluted from the chromatograph at the peak effluent volume of succinic acid, but evaporation of the eluate portion at this effluent volume yielded only a gum which gave color reactions typical of itaconic or citraconic acid and from which no succinic acid could be isolated.

The yields and relative amounts of the ether-extracted acids varied from run to run, the total yield being increased at the expense of the acetone by decreasing the amount of hydrogen peroxide employed. The maximum amount of these acids obtained was 3.0 meq. from 2.00 g. of polylactone.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Rate of Reaction of Phenacyl Halides with 4-Picoline in Benzene Solution

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The quaternization reaction between phenacyl halides and 4-picoline in benzene solution has been found to obey the rate equation: $d\{ArCOCH_2NC_6H_7{}^+Br^-]/dT = k_2[C_6H_7N][ArCOCH_2Br] + k_3[C_6H_7N][ArCOCH_2Br]^2$. The rate constants for the above equation have been evaluated to allow comparison between observed rates of reaction and the reaction coördinate calculated from the rate constants. The activation energy and entropy of activation for the two rate processes have been evaluated.

The work of Baker[1] has shown that the quaternization reaction of phenacyl halides with pyridine exhibits second-order kinetics in solvents of high polarity such as acetone, 90% acetone–water and 90% ethanol–water. The formation of quaternary salts from alkyl halides and pyridine is a second-order reaction in solvents of all degrees of polarity, unless complicated by reverse reaction or heterogeneity.[2]

In the course of an investigation into the energetics of the reaction of phenacyl bromides with pyridine and its homologs, in non-polar solvents, it was observed that the reaction exhibited large deviation from second-order kinetics. This paper deals with the rationalization of the kinetic results obtained from the reaction of *m*-nitrophenacyl bromide, *p*-phenylphenacyl bromide and 2,4,6-trimethylphenacyl bromide with 4-picoline in benzene solution.

Experimental

Materials.—Reagent-grade thiophene-free benzene was distilled from sodium. Acetone was dried over calcium

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[2] (a) N. J. T. Pickles and C. N. Hinshelwood, *J. Chem. Soc.*, 1353 (1936); (b) K. J. Laidler, *ibid.*, 1786 (1938); (c) J. A. Hawkins, *ibid.*, **121**, 1170 (1922); (d) C. G. Swain and R. W. Eddy, THIS JOURNAL, **70**, 2989 (1948).