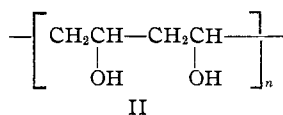
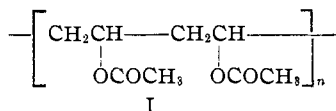


[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Structure of Vinyl Polymers. IX.¹ Catalysts²BY C. S. MARVEL AND E. H. RIDDLE³

Vinyl polymerizations are generally initiated by photochemical activation or by treatment of the monomer with catalysts such as organic peroxides or inorganic halides. These various methods of initiating the reaction chain may lead to activated monomeric or dimeric intermediates of different types and hence may have an influence on the structure of the polymer produced. In order to investigate this possibility, polymers of vinyl acetate, vinyl bromide, vinyl chloride and methyl α -bromoacrylate have been prepared by photochemical activation in the absence of detectable amounts of peroxide and by the action of inorganic halides. The chemical properties of these polymers have been compared with those of the well known polymers produced by peroxide catalysis.

Polyvinyl acetate prepared by peroxide catalysis has been shown to have a "head to tail" structure⁴



(I). A sample of polyvinyl acetate prepared by photochemical activation in the absence of peroxides has been prepared and hydrolyzed to the alcohol. This alcohol is not oxidized by periodic acid and hence must be the 1,3-glycol (II). When a complex of boron fluoride with ether⁵ or with acetic anhydride⁶ was used as a catalyst for the polymerization of vinyl acetate a black insoluble powder which was high in carbon content (76.65%, whereas the vinyl acetate is 55.8%) was obtained. The deep color of the polymer indicates that it contains conjugated unsaturation such as would occur if acetic acid had split out along the chain

(1) For the eighth communication in this series see *THIS JOURNAL*, **62**, 45 (1940).

(2) This material was presented before the Plastics Section of the Paint and Varnish Division, American Chemical Society, Cincinnati, April, 1940.

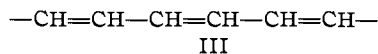
(3) Monsanto Fellow in Chemistry, 1939-1940.

(4) Marvel and Denoon, *THIS JOURNAL*, **60**, 1045 (1938).

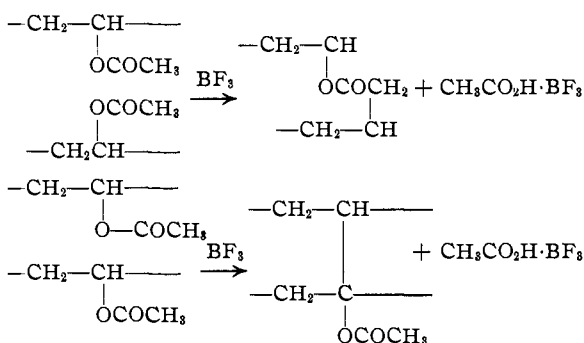
(5) Gasselín, *Ann. chim.*, **3**, 50 (1894).

(6) Meerwein, *Ber.*, **66**, 411 (1933); *J. prakt. Chem.*, **141**, 149 (1934).

during polymerization to produce a complex polyene (III). The insolubility of the product



indicates cross-linking of chains. Such a reaction might occur in a manner similar to certain boron fluoride catalyzed reactions observed by Meerwein.⁶ Thus, if the acetic acid residue in one chain should split out with an active hydrogen of either the carbon or the acetyl residue in a neighboring polymeric unit a cross-linked polymer higher in carbon than the original would result.



It seems likely that the principal part of the molecule must be made up of polyene units with only a little of some such sort of cross-linked structure occurring in the polymer. The high degree of insolubility of this polymer made it unsatisfactory for a study of its reactions.

In an attempt to avoid the side reactions obtained by the use of boron fluoride, toluene diazonium fluoborate was used as catalyst but led to the same black filmy type of polymer which was obtained before.⁷

A soluble polyvinyl acetate was obtained by treating the monomer with cadmium chloride.⁸ The chemical reactions of polyvinyl alcohol from this polymer indicate that it is no different in structure from the polymers obtained with other activating agents.

Similarly methyl α -bromoacrylate was polymerized by photochemical activation and by the

(7) Bruson, U. S. Patent 1,892,101. Dr. C. A. Thomas suggested that we try this catalyst. We are indebted to Dr. G. C. Finger for the sample of catalyst which we used.

(8) Johnson, Barnes and McElvain, *THIS JOURNAL*, **62**, 964 (1940), have shown that this catalyst works well for ketene acetal polymerization.

action of the boron fluoride-acetic anhydride⁶ complex. Both polymers were nearly quantitatively debrominated by reaction with potassium iodide, as determined by titration of the iodine liberated. This is the same result that was obtained with the polymer prepared by peroxide catalysis.⁹

Vinyl bromide was converted to a polymer by exposure to ultraviolet light and by treatment with the boron fluoride-acetic anhydride complex.⁶ These polymers differed somewhat in physical appearance but chemically they behaved alike. Neither liberated iodine from potassium iodide. The polymer obtained by peroxide catalysis gave the same results in this test.¹⁰ When an attempt was made to use the reaction of zinc with these polyvinyl bromides to check the 1,3-dihalide structure the results at first seemed to be confusing as about 95% of the bromine was removed whereas previous experiments had indicated a removal of 87%. Accordingly, a new lot of peroxide catalyzed polyvinyl bromide was prepared. This likewise lost over 90% of its bromine on treatment with zinc. Careful examination of this reaction shows that treatment of polyvinyl bromide with zinc results in removal of bromine by the zinc and also loss of hydrogen bromide from the polymer. The resulting polymer decolorizes potassium permanganate, indicating its unsaturation. Also, the polymers lost a large amount of hydrogen bromide when refluxed with potassium iodide. Hence polyvinyl bromide and zinc will not give a reaction that will be in agreement with the statistical calculations of Flory¹¹ for removal of halogen from polyvinyl halides by zinc. Apparently the greater stability of organic chlorides is responsible for the fact that polyvinyl chloride reacts with zinc to give a saturated molecule. Since over fifty experiments had been run previously with peroxide catalyzed polyvinyl chloride and zinc and in no case had the loss of halogen gone above the amount calculated by the statistical method, those results are still significant. A sample of polyvinyl chloride prepared by photochemical activation lost 72% of its chlorine on treatment with zinc and liberated no iodine when treated with potassium iodide.

These results are all in accord with the view that the nature of the activation of the monomeric vinyl molecule has little to do with the manner in which these monomeric units are arranged in the

final polymer. The structure of the monomeric molecule itself apparently is the factor that determines whether a "head to tail" or "head to head, tail to tail" polymer results.

Experimental

General Methods of Polymerization: With Ultraviolet Light.—The monomer was distilled in a nitrogen atmosphere directly into a tube which was sealed off from the air and placed under the ultraviolet lamp for thirty to forty hours. Peroxide tests with ferrous sulfate and ammonium thiocyanate on distillates of each of the monomers (distilled in nitrogen) were negative. The distillates actually used for the polymerizations were not thus tested since they were directly sealed off in the nitrogen atmosphere after distillation.

With Boron Fluoride Catalysts.—The monomer was distilled into a flask to which the catalyst was added. The flask was allowed to stand at room temperature in the dark; in the case of vinyl acetate, in some experiments the solution was refluxed.

Polymerization of Vinyl Acetate by Ultraviolet Light.—One hundred grams of vinyl acetate was polymerized by exposure to an ultraviolet lamp for twenty-four hours according to directions in the general procedure. The tube was opened, and the polyvinyl acetate was digested with acetone by heating to 50° and stirring with a glass rod. The acetone solution was poured into 500 cc. of water in a 2-liter round-bottomed flask, and steam was passed into the flask rapidly in order to remove the monomer and acetone. The flask was cooled and the liquid decanted from the sticky colorless polymer. The polyvinyl acetate was again dissolved in acetone by refluxing, and the acetone solution was poured into 500 cc. of water in a 2-liter beaker. The liquid was decanted from the polymeric cake, which was transferred to a smaller beaker and dried at room temperature for four days in a vacuum desiccator. The weight of polymer, which still contained a small amount of solvent, was 90 g.

Viscosity measurements according to the Staudinger¹² practice indicated a molecular weight of 23,700.

Mol. Wt. C, 0.0143 molal in thiophene-free benzene; *t*, 24.15 sec. (27°); *K_m*, 2.6×10^{-4} ; for thiophene-free benzene *T*, 22.2 sec. (27°).

A small amount of undissolved polymer remained on the side of the polymerization tube which faced the ultraviolet light. This was dissolved by refluxing with acetone for two days. It was purified as described above, yielding 5 g. of colorless polymer.

Mol. Wt. C, 0.0148 molal in thiophene-free benzene; *t*, 24.60 sec. (27°); mol. wt., 28,050.

Polyvinyl Alcohol from Polyvinyl Acetate Prepared by Ultraviolet Light Treatment.—Eleven grams of the low molecular weight polyvinyl acetate was dissolved in 80 cc. of methyl alcohol. A solution of 0.29 g. of potassium hydroxide in 20 cc. of methyl alcohol was added. After standing overnight, a light yellow gel of polyvinyl alcohol filled the flask. The liquid was decanted and the polymer dissolved by refluxing with distilled water. The aqueous

(12) Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932.

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

(10) Marvel, Sample and Roy, *ibid.*, **61**, 3241 (1939).

(11) Flory, *ibid.*, **61**, 1518 (1939).

solution was poured into acetone with vigorous stirring. Polyvinyl alcohol separated in finely divided flaky form. The solution was filtered through a Buchner funnel and the moist polymer washed with acetone several times. It was then removed from the filter paper while still moist and placed in a beaker in which it was dried in a vacuum desiccator, giving 4 g. of brittle slightly discolored polymer. The saponification number of this polymer was 994, indicating that there is one vinyl acetate unit for every 20.5 vinyl alcohol units in the polymer; *i. e.*, the polymer contained about 4.7% unsaponified units. To a solution of 1 g. of this polyvinyl alcohol in 100 cc. of water was added 100 cc. of 0.1014 *N* periodic acid solution at 0°. No evidence of oxidation of the polyvinyl alcohol could be detected after sixteen hours.

Polymerization of Vinyl Acetate by Cadmium Chloride.—A mixture of 50 cc. of vinyl acetate freshly distilled in a nitrogen atmosphere and 0.2 g. of dry finely powdered cadmium chloride was placed in a flask and sealed in a nitrogen atmosphere. Another flask containing vinyl acetate, but no catalyst, was similarly sealed. Both flasks stood in the dark for two weeks. At the end of this time the solution in the flask containing the cadmium chloride was quite viscous, whereas the viscosity of the other solution appeared to be unchanged and no polymeric material precipitated when it was poured into acetone.

The flask containing the catalyst was opened and the contents poured into acetone, depositing a small amount of polymer which was purified by dissolving in boiling acetone, pouring into water to precipitate the polymer, decanting the liquid and repeating this procedure twice more. The polymer was then dried in a vacuum desiccator, giving 5 g. of colorless brittle polymer.

Mol. Wt. *C*, 0.01163 molal in thiophene-free benzene; *t*, 23.50 sec. (27°); mol. wt., 19,400.

Polyvinyl Alcohol from Polyvinyl Acetate from Cadmium Chloride.—Four grams of the cadmium chloride catalyzed polyvinyl acetate was alcoholized by 0.15 g. of potassium hydroxide in methanol in the manner described above for the ultraviolet catalyzed polymer. Two grams of brittle polyvinyl alcohol was obtained. This material had a saponification number of 1112, indicating about 4.1% unsaponified vinyl acetate units. A sample of this polyvinyl alcohol was not oxidized by periodic acid after forty-nine hours.

Polymerization of Vinyl Acetate by Boron Fluoride Complexes.—To a solution of 25 cc. of freshly-distilled vinyl acetate in 50 cc. of freshly-distilled carbon tetrachloride was added 0.5 cc. of the boron trifluoride-ether complex (b. p. 125–126°). After refluxing for half an hour, the solution darkened considerably. Refluxing was continued for five hours. The carbon tetrachloride and unchanged vinyl acetate were distilled off; the black residue was refluxed with a large amount of acetone and the mixture filtered, giving a brown filtrate and 2 g. of black residue. The filtrate was poured into petroleum ether, precipitating a dark brown powder. This was removed by filtration, washed with petroleum ether and dried by suction. It weighed 1 g. This material was refluxed with absolute alcohol for three hours. The solution turned light brown, but when the mixture was filtered the residue weighed 1 g.

A solution of 10 cc. of freshly-distilled vinyl acetate in 20 cc. of freshly-distilled toluene was refluxed with four drops of freshly-prepared boron trifluoride-ether complex for twelve hours. The black mixture was cooled and poured into petroleum ether. The black precipitate was removed by filtration, washed with petroleum ether and dried, giving 2.5 g. of gray finely-divided powder. However, this was also insoluble in alcohol.

A mixture of 15 cc. of distilled vinyl acetate and ten drops of boron trifluoride-ether complex was let stand in a tightly-stoppered flask at room temperature (24–27°) for one week. The solution turned dark; filtration gave 2 g. of black powder which was insoluble in alcohol.

A solution of 40 cc. of distilled vinyl acetate in 40 cc. of distilled toluene was refluxed with 0.5 g. of the complex from acetic anhydride and boron trifluoride⁶ for twelve hours. Petroleum ether was added to the dark solution and the mixture filtered. The yield of air-dried black shiny powder was 5 g.

Anal. Calcd. for $C_4H_6O_2$: C, 55.80; H, 6.98. Found: C, 76.65; H, 7.80.

All of these products were practically insoluble in alcohol. Boiling with alcoholic alkali left products which were highly colored and were insoluble in water. Hence no tests for oxidation with periodic acid could be made.

Polymerization of Vinyl Acetate with Toluene Diazonium Fluoborate Catalyst.—In each of two 125-cc. Erlenmeyer flasks was placed 30 cc. of vinyl acetate freshly distilled in a nitrogen atmosphere, 30 cc. of freshly distilled thiophene-free benzene, and 0.1 g. of toluene diazonium fluoborate.

The contents of one of the flasks was refluxed for six hours. After two hours of this time, the solution turned black. When the solution had cooled, it was poured into petroleum ether and let stand overnight. The liquid was decanted from the film of polymer which had deposited on the bottom of the flask, and methanol was added. After standing overnight at room temperature, the film was loosened and cut up into small pieces; the solution was refluxed for three days and then filtered, giving a dark filtrate and 4 g. of filmy sticky residue. This polymer could not be hydrolyzed to a water-soluble polyvinyl alcohol.

The other flask was allowed to stand in the dark at room temperature for two weeks. The contents of the flask was poured into petroleum ether but no polymer separated. Evaporation to dryness gave no appreciable residue.

Polymerization of Methyl α -Bromoacrylate by Ultraviolet Light.—A solution of 15 g. of methyl α -bromoacrylate in 20 cc. of peroxide-free dioxane was placed in a quartz test-tube and exposed to a mercury vapor lamp. After irradiation by ultraviolet light for forty hours, the solution was quite viscous. Ether was added and stirred into the viscous solution with a stirring rod, the polymer separating as a white powder. The solution was filtered, the polymer washed with ether and dried under reduced pressure. The yield was 14 g.

Mol. Wt. *t* for pure dioxane at 28°, 35.80; *C*, 0.01315 in dioxane; *t*, 36.7 sec. (28°); *K_m*, 1.7×10^{-4} ; mol. wt., 11,230.

Debromination of the Ultraviolet Catalyzed Polymer of Methyl α -Bromoacrylate.—To a solution of 3 g. of the

polymer in 100 cc. of freshly-distilled acetone was added 3 g. of potassium iodide. The mixture was refluxed for three days, during which time a precipitate appeared and the solution turned deep red. Ten cubic centimeters of this solution was withdrawn and titrated with 0.107 *N* sodium thiosulfate, of which 10 cc. was required. This corresponds to removal of about 85% of the bromine from the polymer of methyl α -bromoacrylate.

Polymerization of Methyl α -Bromoacrylate with the Boron Fluoride-Acetic Anhydride Complex.—Twenty-five grams of methyl α -bromoacrylate, freshly prepared in a nitrogen atmosphere by distillation from a quinoline and methyl α,β -dibromopropionate mixture, was dissolved in 25 cc. of freshly-distilled peroxide-free toluene and 2 g. of the complex from boron fluoride and acetic anhydride⁶ was added. The flask was stoppered tightly and let stand at room temperature in the dark for one week. At the end of this time ether was added to the solution. The gummy light brown mass which precipitated was dissolved in dioxane, the solution was filtered and the filtrate poured into ether. The colorless powdery polymer was removed by filtration, washed with ether and dried in a vacuum desiccator. The yield was 10 g.

Anal. Calcd. for $C_4H_5O_2Br$: Br, 48.48. Found: Br, 48.66.

Mol. Wt. *C*, 0.01230 molal in dioxane; *t*, 36.30 sec. (28°); mol. wt., 6700.

Treatment of the Boron Fluoride Catalyzed Polymer of Methyl α -Bromoacrylate with Potassium Iodide.—To a solution of 0.332 g. of the polymer in 50 cc. of peroxide-free dioxane was added 5 cc. of a 30% aqueous solution of potassium iodide. The mixture was refluxed gently for three days, after one day becoming red in color. The solution was cooled and titrated, requiring 19.11 cc. of 0.1000 *N* sodium thiosulfate. This corresponds to removal of 95% of the bromine in the polymer.

Polymerization of Vinyl Bromide by Ultraviolet Light.—By warming to room temperature, crude vinyl bromide was distilled from a 125-cc. Erlenmeyer flask through a small upright condenser into a tube which was drawn to capillary size and led half way down a 200 \times 25 mm. test-tube to which had been attached a foot-long (31-cm.) neck of 6-mm. tubing. The test-tube was immersed in dry-ice-acetone to condense the vinyl bromide. A slow stream of nitrogen was run through the apparatus. After 20 cc. of vinyl bromide had collected, distillation was stopped by immersing the Erlenmeyer flask in dry-ice-acetone. The capillary lead-in tube was withdrawn and immediately the test-tube was sealed off and was placed under the ultraviolet lamp for twenty hours. The tube was then opened and the unchanged monomer allowed to evaporate. The polymer, weighing 13 g., was left as a brittle powder which turned dark on standing. It was soluble in benzene and in dioxane, only after refluxing, and the solutions were colored. Because of these difficulties no attempts were made to determine viscosity and molecular weight.

Polymerization of Vinyl Bromide by Boron Fluoride Catalyst.—To 15 cc. of freshly-distilled vinyl bromide in a 50-cc. Erlenmeyer flask was added a solution of 1 g. of the compound from acetic anhydride and boron fluoride⁶ in toluene. The tightly stoppered flask was kept at

0–10° for one month and then at room temperature for three weeks. A precipitate of dark gray powder was removed by filtration, washed with ether and dried under reduced pressure. The yield was 1.8 g.

Reaction of Zinc with Polyvinyl Halides.—The procedure was identical in all cases. The sample of polyvinyl halide was dissolved in peroxide-free dioxane and a large excess of purified zinc dust (2–4 g.) was added. The solutions were refluxed rapidly to keep the zinc moving, and at two-day intervals about 0.5 g. of purified zinc was added through the reflux condenser, which carried a calcium chloride tube at the top. Total reflux time in each case was approximately one hundred and forty hours. At the end of this time, the solutions were cooled, the zinc removed by filtration and washed with dioxane, and the filtrate (including washings) titrated for halogen by the Volhard method.

TABLE I

Halogen Catalyst	Polymer, g.	Hal. present, g.	<i>N</i> AgNO ₃ required, cc.	Hal. removed, g.	Hal. removed, %
Br UV Light	0.4188	0.3128	3.788	0.3025	96.5
Br UV Light	.4956	.3702	4.330	.3460	93.5
Br UV Light	.2450	.1830	2.163	.1728	94.5
Br UV Light	.2563	.1914	2.291	.1830	95.5 ^a
Br Peroxide	.1604	.1198	1.0775	.08608	72
Br Peroxide	.1854	.1385	1.691	.1351	96.8
Br BF ₃	.0978	.0730	0.731	.0584	80
Cl Peroxide	.1012	.0574	1.218	.04323	76
Cl UV Light	.1044	.0593	1.205	.0428	72.1

^a This run was used for an unsaturation test. After removing the zinc by filtration, the filtrate was made up to exactly 100 cc. with dioxane. A 10-cc. sample was removed with a pipet and shaken with 2 cc. of a 1% solution of potassium permanganate in dioxane to which two drops of distilled water had been added to dissolve the permanganate. After shaking for about one minute, the permanganate color disappeared. The remaining 90 cc. of the dioxane solution from the zinc treatment was titrated for halogen, adding 10% to the value obtained in order to account for the 10 cc. removed for the unsaturation test. This showed that 95.5% of the bromine had been removed by zinc.

Treatment of Polyvinyl Bromide with Potassium Iodide.—To a solution of 0.200 g. of ultraviolet catalyzed polyvinyl bromide in 100 cc. of peroxide-free dioxane was added 1 g. of potassium iodide. The solution was refluxed vigorously for three days. The solution developed a red-brown color, but when the solution was cooled, diluted with 50 cc. of water and filtered, the filtrate was colorless and gave a negative starch test, showing that no iodine was present. The brown residue was washed with water, ethyl alcohol and ether, and was dried in a vacuum desiccator. The analysis showed that a large amount of bromine had been removed from the polymer.

Anal. Calcd. for C_2H_3Br : Br, 74.7. Found: Br, 59.34.

When a dioxane solution of boron fluoride catalyzed polyvinyl bromide was refluxed with potassium iodide, no iodine was liberated and when the solution was diluted with water as before, a similar brown polymer separated.

Summary

Evidence has been presented to show that vinyl polymers formed by the action of catalysts such as peroxides and boron fluoride or by photochemical activation have the same arrangement of monomeric units in the polymer chain. The nature of the monomer unit determines whether the polymer is of the "head

to tail" or "head to head, tail to tail" variety.

Vinyl acetate loses acetic acid when polymerized by the action of boron fluoride complexes and the polymer is intractable.

Polyvinyl bromide loses hydrogen bromide as well as bromine when heated with zinc and hence this reaction is not useful for determining structure in this case.

URBANA, ILLINOIS

RECEIVED JULY 12, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

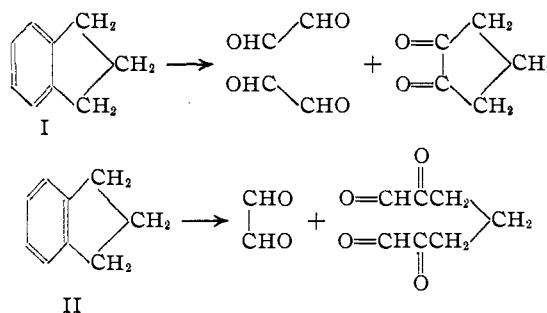
Ozonization of Hydrindene

BY LOUIS LONG, JR.,¹ AND LOUIS F. FIESER

While Lothrop² has shown that bond fixation comparable to that associated with the unique chemical characteristics of naphthalene derivatives³ does not exist in the hydrindene series, recent studies of competition reactions⁴ and of relative reactivities⁵ indicate that there is a certain qualitative differentiation, with respect to stability or abundance, between the two Kekulé forms and that this is in the direction predicted by Mills and Nixon.⁶ The use of derivatives of a hydrocarbon for the investigation of bond structure of course introduces some element of uncertainty because of the possibility that the substituent may stabilize one of the Kekulé forms.⁷ In the case of hydrindene, where any differentiation is likely to be a subtle one, this consideration may be of some importance.

The method of ozonization, first applied to the problem of bond structure by Levine and Cole,⁸ has been investigated as a possible means of gaining information concerning the hydrocarbon itself. Levine and Cole obtained from *o*-xylene fragments establishing the presence in the starting material of both possible Kekulé forms. Hydrindene would likewise be expected to give rise to products characteristic of the arrangement of the double bonds. As the primary products, the preferred structure I (in terms of the Mills-Nixon hypothe-

sis) should yield two moles of glyoxal and one of cyclopentanedione-1,2, while the alternate structure II should yield glyoxal and α, α' -diketopimelic dialdehyde.



The ozonization of hydrindene proceeded satisfactorily in ethyl chloride at -30° or in acetic acid at room temperature, and the proportion of ozone unabsorbed was comparable with that observed with benzene and naphthalene.⁹ The ozonide showed a tendency to decompose explosively only when produced in ethyl acetate or acetic anhydride solution. Of the various methods tried for decomposing the ozonide the catalytic hydrogenation process of F. G. Fischer¹⁰ seemed by far the most satisfactory. The solution resulting from ozonization in acetic acid could be submitted directly to hydrogenation, and on employing ethyl chloride this solvent could be distilled without difficulty, after removal of traces of free ozone, and replaced by alcohol for the hydrogenation. The reaction mixtures were processed by distillation, crystallization, and the formation of carbonyl derivatives.

(1) Present address: Cobb Chemical Laboratory, University, Virginia.

(2) Lothrop, *THIS JOURNAL*, **62**, 132 (1940).

(3) Fieser and Lothrop, *ibid.*, **57**, 1459 (1935).

(4) Lindner and co-workers, *Monatsh.*, **72**, 354, 355, 361 (1939).

(5) Baker, *J. Chem. Soc.*, 476 (1937); McLeish and Campbell, *ibid.*, 1103 (1937); Sandin and Evans, *THIS JOURNAL*, **61**, 2916 (1939).

(6) Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).

(7) Fieser and Seligman, *THIS JOURNAL*, **60**, 173, note 18 (1938).

(8) Levine and Cole, *ibid.*, **54**, 338 (1932).

(9) Brus and Peyresblanques, *Compt. rend.*, **190**, 501, 685 (1930).

(10) F. G. Fischer, Düll and Ertel, *Ber.*, **65**, 1468 (1932).