

tate and which on the basis of its crystalline structure, solubility in different solvents, as well as of a mixed melting point determination, was found to be identical with a specimen of N-3-methyl-5-benzylhydantoin-N-1-acetic acid which had been prepared synthetically.<sup>2</sup>

### Summary

$\beta$ -Phenylalanine-N-acetic acid belongs to the class of imino-dibasic acids and resembles imino-diacetic acid in many respects although some of its derivatives are much less stable. It is the only acid of this class which has as yet been described as forming an acyclic ureide under

the direct action of potassium cyanate.

Although, on the basis of theoretical considerations, ring closure with the elimination of one molecule of water should result in the formation of two isomeric hydantoinis characterized by different acid groups in the -N-1-position, only one such compound was obtained when the dipotassium salt of the acyclic ureide was treated with hydrochloric acid. The formation of the isomer under entirely different conditions will be described in a later paper.

SOUTH HADLEY, MASS.

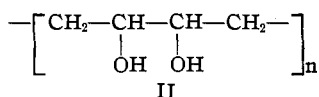
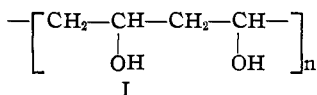
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## The Structure of Vinyl Polymers. II.<sup>1</sup> Polyvinyl Alcohol

BY C. S. MARVEL AND C. E. DENOON, JR.<sup>2</sup>

The peroxide catalyzed polymerization of vinyl compounds produces linear polymers of considerable technical importance but the exact structures of these polymers have not received much attention. Staudinger<sup>3</sup> prepared polyvinyl alcohol from polyvinyl acetate and ascribed to these polymers the 1,3-glycol (and ester) structure (I). In a later article<sup>4</sup> the statement was made that oxalic and succinic acids were oxidation products of polyvinyl alcohol. The formation



of oxalic acid from the polymeric 1,3-glycol (I) would be expected, but it is difficult to see how succinic acid could be formed from this structure. On the other hand, succinic acid would be the expected oxidation product of the polymeric 1,2-glycol structure (II) which is a second possible structure for polyvinyl alcohol. Staudinger, Frey and Stark<sup>4</sup> have obtained some acetaldehyde by heating polyvinyl alcohol to 200°. Herrmann and Haehnel<sup>5</sup> have reported iodoform as a product of the action of sodium hypoiodite on polyvinyl

alcohol. Both reactions indicate that the 1,3-glycol structure (I) is the correct formulation for the polymer. Thus, the evidence now available in the literature may be said to indicate that polyvinyl alcohol contains both 1,2- and 1,3-glycol units.

We have tried to repeat the nitric acid oxidation of polyvinyl alcohol to yield oxalic and succinic acids. However, oxalic acid was the only product which we obtained. It is interesting to note that anhydrous oxalic acid melts at 189° and in our work was first mistaken for succinic acid (m. p. 188°). Since no experimental details of the earlier isolation of succinic acid<sup>4</sup> are recorded it is possible that the earlier investigators made the same error which we first made.

Periodic acid has been shown<sup>6</sup> to be a specific oxidizing agent for 1,2-glycols. Hence if there are any 1,2-glycol units in polyvinyl alcohol it should be possible to detect them with this reagent.<sup>7</sup> Accordingly a 0.2 M (based on  $(-\text{CH}_2-\text{CHOH}-)_2$  as the unit) solution of polyvinyl alcohol was treated with a standardized solution of periodic acid at 0° and samples were withdrawn and titrated from time to time to determine whether any oxidation had occurred. No evidence of any oxidation was found although the experiment was continued for thirteen hours. As

(1) For the first communication on this topic see Marvel and Levesque, *THIS JOURNAL*, **60**, 280 (1933).

(2) Du Pont Fellow in Chemistry.

(3) Staudinger, *Ber.*, **59**, 3019 (1926).

(4) Staudinger, Frey and Stark, *ibid.*, **60**, 1782 (1927).

(5) Herrmann and Haehnel, *ibid.*, **60**, 1658 (1927).

(6) (a) Malaprade, *Compt. rend.*, **186**, 382 (1928); *Bull. soc. chim.*, [5] **1**, 833 (1934); (b) Fleury and Fatome, *J. pharm. chim.*, [8] **21**, 247 (1933); (c) Karrer and Hirohata, *Helv. Chim. Acta*, **16**, 959 (1933); (d) Jackson and Hudson, *THIS JOURNAL*, **59**, 2049 (1937).

(7) The use of periodic acid for this purpose was suggested to the authors by Dr. G. J. Berchet.

a check on this experiment similar mixtures were prepared using 2,3-butanediol, 2,4-pentanediol,<sup>8</sup> and soluble starch in place of polyvinyl alcohol. The 2,3-butanediol was completely oxidized by the periodic acid in fifteen minutes. The 2,4-pentanediol was unaffected in thirteen hours. Starch had used up about two-thirds of the expected amount of periodic acid in thirteen hours. Jackson and Hudson<sup>6d</sup> previously had shown that starch is oxidized by periodic acid without complete depolymerization. The above experiments show the similarity of behavior between polyvinyl alcohol and a known 1,3-glycol. The fact that no periodic acid is used up in thirteen hours is evidence that no 1,2-glycol unit is present in the polymeric molecule. The results of these experiments are shown graphically in Fig. 1.

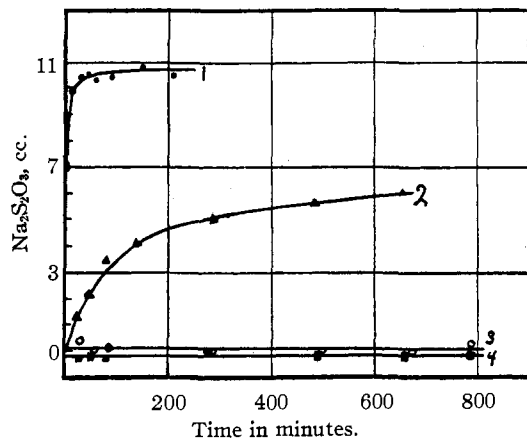
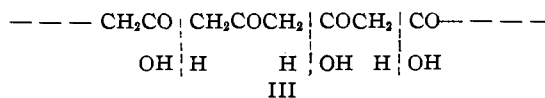


Fig. 1.—Curve 1, 2,3-butanediol; 2, starch; 3, polyvinyl alcohol; 4, 2,4-pentanediol.

Herrmann and Haehnel<sup>5</sup> have stated that polyvinyl alcohol apparently is not oxidized by chromic acid. We found that when a water solution of polyvinyl alcohol was treated in acid solution with just the theoretical amount of potassium dichromate required to oxidize the alcohol groups to ketone groups, two-thirds of the dichromate was used up in ten minutes and the reaction was complete in two hours. When this reaction mixture was made alkaline by the addition of sodium hydroxide and boiled under a reflux condenser, both acetone and acetic acid were produced. This obviously is the familiar alkaline cleavage of a 1,3-diketone (III). Some of the acetic acid thus obtained may have come from traces of polyvinyl acetate in the original polyvinyl alcohol.

(8) We are indebted to Professor Homer Adkins for this compound.



A third line of evidence that polyvinyl alcohol is a 1,3-glycol was obtained by a study of the ultraviolet absorption spectra of 2,4-pentanediol and polyvinyl alcohol. Both show absorption maxima in the neighborhood of 2750 Å. (Fig. 2) whereas 2,3-butanediol does not absorb in the ultraviolet.<sup>9</sup>

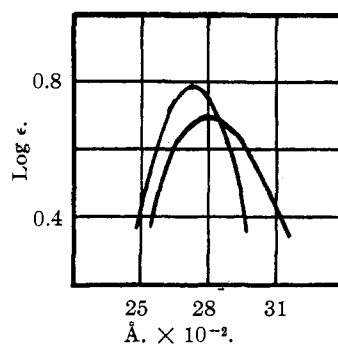


Fig. 2.—Upper curve, 2,4-pentanediol; lower curve, polyvinyl alcohol.

Other reactions of polyvinyl alcohol which were studied support the view that it is a 1,3-glycol. When a water solution of polyvinyl alcohol was treated with boric acid with the intention of studying the conductivity of the solution after the manner of Böeseken<sup>10</sup> an insoluble boric acid complex was precipitated. This complex was not a definite product but was apparently formed by some random cross-linking of the linear polymeric chains through complex formation. It was possible to prepare gelatinous sodium and calcium salts of these boric acid complexes but their analyses did not enable us to assign definite formulas to the products.

In view of the successful preparation of acetals<sup>5</sup> from polyvinyl alcohol, an attempt was made to make esters of a related type. An ester interchange reaction with diethyl oxalate gave an extremely insoluble product which obviously had cross-linkages between polymeric chains as might be expected since a 1,3-glycol would have to yield at least a seven-membered cyclic ring if cross-linking did not occur. A saponification number on the insoluble ester indicated that about 8% of the hydroxyl groups were esterified. By

(9) We are indebted to Mr. E. C. Kirkpatrick for aid in obtaining these data and for their interpretation.

(10) J. Böeseken, *Ber.*, **46**, 2612 (1913).



40.5 vinyl alcohol units. In other words, the polyvinyl alcohol contained about 2.5% of unsaponified ester units.

*Anal.* Calcd.: C, 54.54; H, 9.12. Found: C, 54.78; H, 9.64.

**Oxidation of Polyvinyl Alcohol with Nitric Acid.**—Five grams of polyvinyl alcohol was dissolved in 500 cc. of water and 35 cc. of concentrated nitric acid was added. The solution was evaporated to dryness on a steam-cone, the residue extracted with ether and the ether evaporated on the steam-cone. The crystalline residue was recrystallized from water. This product melted at 101° and a mixture of it and a sample of hydrated oxalic acid melted at 100°. The material gave a neutral equivalent of 62.7 (calcd. for hydrated oxalic acid, 63).

**Oxidations with Periodic Acid.**—Solutions were made up containing the following amounts of polyhydroxy compounds in 500 cc. of water: polyvinyl alcohol, 8.8 g.; 2,3-butanediol, 9 g.; 2,4-pentanediol, 10.4 g.; and starch, 16.2 g. A 50-cc. sample of each of these solutions was placed in a 200-cc. flask and cooled in an ice-bath. To each was added 100 cc. of 0.1081 *M* periodic acid, which had been previously cooled, and the contents mixed. A 10-cc. sample was withdrawn and immediately titrated by the potassium iodide-thiosulfate method. Other samples were withdrawn and titrated at intervals over a period of thirteen hours. The following table gives the results in terms of cc. of 0.1301 *N* thiosulfate used up.

Both in this table and in Fig. 1 the value for the term "cc. of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>" is obtained by subtracting the titration value from the titer, which would be calculated if no oxidation had occurred and hence is a measure of the oxidation which has taken place. The reduction of one mole of periodic acid per glycol unit corresponds to 10.25 cc. of 0.1301 *N* thiosulfate solution.

TABLE I

## OXIDATION OF VARIOUS GLYCOLS WITH PERIODIC ACID

Polyvinyl Alcohol		Starch		2,4-Pentanediol		2,3-Butanediol	
Time, min.	Cc. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Time, min.	Cc. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Time, min.	Cc. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Time, min.	Cc. Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>
0	0	0	0	0	0	0	6.90 <sup>a</sup>
31	0.35	25	1.3	26	-0.30	15	10.00
57	0	48	2.20	49	-.20	30	10.42
87	0.10	80	3.40	81	-.20	45	10.52
292	0	140	4.10	287	.05	60	10.35
500	0	287	5.00	488	-.05	90	10.48
675	0	480	5.75	663	-.10	150	10.78
790	0.30	655	6.05	778	-.05	210	10.52
		770	6.95				

<sup>a</sup> The oxidation already had proceeded to this stage before a sample could be withdrawn and titrated.

**Oxidation of Polyvinyl Alcohol by Potassium Dichromate.**—A solution was made up containing 11.88 g. of potassium dichromate and 25 cc. of sulfuric acid and diluted to 250 cc. with water. A titration of a 5-cc. portion of this solution used up 37.50 cc. of 0.1301 *N* sodium thiosulfate. To 150 cc. of an aqueous solution, containing 2.65 g. of polyvinyl alcohol, was added 125 cc. of the above dichromate solution. Five cc. samples of this oxidation mixture were withdrawn at intervals and titrated with 0.1301 *N* sodium thiosulfate. The results are given in Table II.

TABLE II

## OXIDATION OF POLYVINYL ALCOHOL WITH POTASSIUM DICHROMATE

Time in minutes	10	130
Dichromate used up in terms of cc. of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	9.75	16.55

The term "cc. of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>" has the same significance as in Table I. The complete reduction of the dichromate corresponds to 17.05 cc. of sodium thiosulfate.

**Oxidation of Polyvinyl Alcohol and Subsequent Alkaline Hydrolysis.**—To a solution of 5.28 g. of polyvinyl alcohol in 100 cc. of water was added slowly a solution of 11.88 g. of potassium dichromate and 25 cc. of concentrated sulfuric acid in 50 cc. of water. The mixture was cooled in an ice-bath to prevent an excessive rise in temperature. After making alkaline with solid sodium hydroxide, an additional 15 g. of sodium hydroxide was added and the mixture which now contained a large precipitate was refluxed for eighteen hours. The mixture was distilled until 50 cc. was obtained and the distillate treated with 2,4-dinitrophenylhydrazine reagent. The yellow precipitate which formed was filtered off, washed with water, and dried in a vacuum desiccator. It weighed 0.1 g. and on recrystallization from ethyl alcohol and ethyl acetate melted at 125°. A mixture of this material with the 2,4-dinitrophenylhydrazone of acetone melted at 125°. The residue left after the acetone had been distilled off was made acidic with phosphoric acid and 75 cc. was distilled. This distillate was diluted with water to 150 cc. A 10-cc. sample of this solution needed 16.35 cc. of 0.00626 *N* alkali for neutralization. The Duclaux numbers on the remainder were found to be 6.31, 6.63, and 6.72 (accepted values for acetic acid, 6.8, 7.1, and 7.4).<sup>14</sup>

**Ultraviolet Absorption Spectra of the Various Glycols.** (By E. C. Kirkpatrick.)—The spectra were taken on a Bausch and Lomb ultraviolet spectrograph. A hydrogen discharge tube operating on 15,000 volts gave a continuous ultraviolet source. The observation of the H<sub>α</sub>, H<sub>β</sub>, and H<sub>γ</sub> lines served to calibrate the wave length scale of the instrument. Wratten and Wainwright Process Panchromatic dry plates were used. The pictures were taken with a slit opening of 60 μ × 5 mm. and a 1-cm. cell. The absorption coefficient was determined by comparing with the blackness of a trace due to a solution of naphthalene, 10<sup>-4</sup> molar, whose spectrum has been well measured. Concentrations, which were 0.1 *M* in glycol units, were found to be satisfactory. Figure 2 shows the maxima which polyvinyl alcohol and 2,4-pentanediol exhibit. Under these conditions, 2,3-butanediol does not absorb in the ultraviolet region.

**Polyvinyl Alcohol-Boric Acid Complex.**—Two grams of polyvinyl alcohol was dissolved in 100 cc. of hot water, filtered from any insoluble material and then poured into a solution of 2 g. of boric acid in 50 cc. of water. A white dough-like solid separated, which, after filtering and drying in a vacuum desiccator weighed 0.8 g.

*Anal.* Found: C, 38.15; H, 12.62.

A solution of 1.7 g. of polyvinyl alcohol in 100 cc. of

(14) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1935, p. 66.

water was added to a hot solution containing 0.5 g. of sodium hydroxide and 0.7 g. of boric acid in 50 cc. of water. On cooling in the refrigerator, the solution set to a gel. The gel was triturated twice with 95% alcohol, twice with absolute alcohol, and twice with ether; it was then dried in a vacuum desiccator. The white amorphous powder weighed 1.7 g.

*Anal.* C, 36.42; H, 6.26; Na, 10.13; B, 4.89.

After the ignition to obtain a carbon-hydrogen analysis a residue always remained. This was weighed, assumed to be sodium borate and the values for sodium and boron were approximated in this manner.

A calcium salt was prepared by adding calcium chloride solution to a water solution of the sodium salt. The solution was then heated, stirred, and the product was isolated and analyzed in a manner similar to that described for the sodium salt.

*Anal.* Found: C, 36.10; H, 7.12; B, 3.78; Ca, 6.94.

**Oxalate of Polyvinyl Alcohol.**—Three grams of polyvinyl alcohol and 10 g. of diethyl oxalate were heated at 140–160° for two and one-half hours in a flask equipped with a short air condenser so that the ethyl alcohol could boil out. The light colored solid was filtered, washed thoroughly with ether and dried in a vacuum desiccator. It weighed 2.6 g. and was insoluble in the common organic solvents. It gave a saponification equivalent of 571. Since the polyvinyl alcohol unit has a molecular weight of 44 and the half oxalate unit has a molecular weight of 71, this saponification equivalent shows that roughly 8.1% of the hydroxyl groups in the polymer were esterified in this reaction.

A small portion of the ester was treated at room temperature with chloroacetyl chloride for several hours. The mixture was then poured into water, the solid filtered off, washed well with cold water and dried in a vacuum desiccator. This material contained 24.57% chlorine. This chlorine analysis indicates that the original ester interchange esterified 25% of the hydroxyl groups in the polyvinyl alcohol.

An attempt was also made to prepare the oxalate of polyvinyl alcohol from oxalyl chloride and the sodium derivative of the polymer. A solution of 1.76 g. of polyvinyl alcohol in 150 cc. of liquid ammonia was mixed with a solution of 0.92 g. of sodium in 50 cc. of the same solvent. A bluish precipitate, which soon turned white, separated immediately. The ammonia was allowed to evaporate and the residual cream colored solid was suspended in dry xylene and treated with oxalyl chloride. No definite organic products could be isolated from this reaction mixture.

**Bromination Product of Polyvinyl Alcohol.**—The bromination was carried out in such a manner that (1) the bromine used, (2) the bromide ions produced, and (3) the organic bromine produced could be determined. A sample of polyvinyl alcohol was weighed into a beaker, dissolved in 300 cc. of hot water and filtered into a 1-liter volumetric flask. A weighed amount of bromine was cooled in ice and added to the cooled solution. The solution was diluted to 1 liter with water, shaken thoroughly and allowed to stand for three days. A yellow flocculent precipitate formed and settled to the bottom. A 10-cc. sample of the supernatant liquid was withdrawn and titrated

with thiosulfate solution. Another 10-cc. sample was withdrawn and titrated for total bromine by means of silver nitrate and ammonium thiocyanate solutions. The amount of bromide ion could then be calculated by difference. The yellow precipitate was filtered into a sintered glass crucible and washed with a very small amount of alcohol. After drying, it was weighed and then analyzed for bromine. A summary of the results is given in Table III.

TABLE III

REACTION OF POLYVINYL ALCOHOL WITH BROMINE AND WATER

Run no.	5	6	Av.
Polyvinyl alcohol, g.	1.76	1.76	
Moles of polyvinyl alcohol in (CH <sub>2</sub> CHOH) <sub>n</sub> unit	0.020	0.020	
Bromine, g.	13.217	13.163	
Equivalents of bromine	0.1655	0.1647	
Equivalents of bromine unused	.0717	.0712	
Equivalents of (Br) <sup>-</sup> produced	.0661	.0638	
Weight of precipitate, g.	3.388	3.372	
Per cent. of bromine in ppt.	50.55	48.90	49.73
Equiv. of organic bromine	0.0216	0.0206	
Ratio bromide ion/organic bromine	3.06	3.10	3.08
Balance error, %	3.7	5.5	4.6

Calcd. for (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>Br)<sub>n</sub>: C, 29.11; H, 3.03; Br, 48.46.  
Found: (not the same sample as in Run 5 or 6) C, 28.00; H, 3.01; Br (average of Runs 5 and 6), 49.73.

**Attempted Bromination of the Bromination Product.**—One gram of the bromination product (containing 50.38% bromine) was dissolved in 100 cc. of dioxane and filtered. Two cubic centimeters of water and 5 g. of bromine were added and the mixture allowed to stand for three days. The solution was then evaporated at room temperature to a sirup. Methyl alcohol was added producing a yellow precipitate, which was filtered out, washed with methyl alcohol, and dried in a vacuum desiccator. It weighed 0.2 g.

*Anal.* Found: Br, 50.72.

**Acetylation of the Bromination Product.**—One gram of the bromination product was dissolved in a mixture of 50 cc. of acetic anhydride and 20 cc. of dioxane, the solution filtered and allowed to stand for two days. The solution was evaporated to dryness at room temperature, redissolved in a little dioxane, filtered and precipitated by the addition of methyl alcohol. It was then filtered, washed with methyl alcohol and dried in a vacuum desiccator (weight, 0.63 g.).

*Anal.* Calcd. for (C<sub>6</sub>H<sub>7</sub>O<sub>3</sub>Br)<sub>n</sub>: C, 34.80; H, 3.38; Br, 38.63. Found: C, 32.58; H, 2.75; Br, 36.41.

**Action of the Silver Salt of *p*-Nitrobenzoic Acid on the Bromination Product.**—The silver salt was made from 1.25 g. of the potassium salt of *p*-nitrobenzoic acid and suspended in 100 cc. of dioxane solution which contained 0.82 g. of the bromination product. The mixture was shaken for thirty-five hours, the precipitate filtered off, washed with a little dioxane, and the filtrate was evaporated to dryness at room temperature, yielding a dark colored residue. This was extracted with 100 cc. of hot absolute

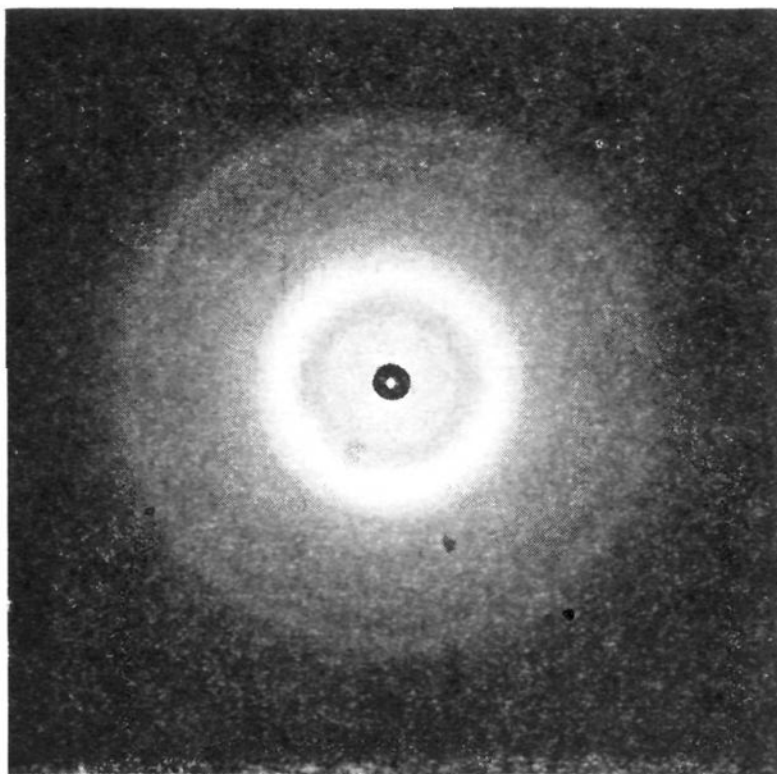


Fig. 3.

alcohol and the extract evaporated at room temperature to give a yellow residue, which after drying in a vacuum desiccator weighed 0.75 g.

*Anal.* Calcd. for  $(C_{11}H_9O_6N)_n$ : N, 5.58. Found: N, 4.90; Br, 9.28.

The nitrogen analysis indicates that 88% of the bromine was replaced by the *p*- $NO_2C_6H_4CO_2$ -group, whereas the bromine content indicates that 81% has been replaced in this reaction.

**Hydrolysis of the Bromination Product.**—A mixture of 0.5 g. of the bromination product (containing 50.74% bromine) and 50 cc. of water was heated under reflux on a steam-cone for twelve hours. The material, which looked essentially unchanged, was filtered off, washed thoroughly with water and dried in a vacuum desiccator. It weighed 0.33 g.

*Anal.* Found: Br (original bromination product), 50.74, (hydrolyzed product) 45.53.

A solution was made up of 1 g. of the bromination product in 80 cc. of dioxane, 20 cc. of water added, the mixture filtered and allowed to stand two days. The solution was evaporated to dryness at room temperature and extracted with dioxane. On adding water, a yellow precipitate formed which was filtered off and washed with water. After drying in a vacuum desiccator, it weighed 0.59 g.

*Anal.* Found: Br, 39.28.

**Chlorination of Polyvinyl Alcohol.**—Chlorine was bubbled very slowly for forty-eight hours through a solution of polyvinyl alcohol (3.52 g. in 350 cc. of water). A brown rubbery mat and a white flocculent precipitate were formed. The white precipitate was poured off with the mother liquor, leaving the mat behind. The brown material on transferring to a desiccator turned black and was not further investigated. The white precipitate was filtered off, washed with water and dried in a vacuum desiccator. It weighed 0.25 g.



Fig. 4.

*Anal.* Calcd. for  $(C_4H_6O_2Cl)_n$ : Cl, 29.46. Found: Cl, 31.74.

**X-Ray Analysis.** (By S. T. Gross).—The patterns were obtained by means of a Philips Metalix tube, having a copper target, and using 20 milliamperes and 30 kilovolts. The samples were exposed for three hours at a distance of 3 cm. Agfa film was used. The various lines with their corresponding interplanar distances are given below.

POLYVINYL ALCOHOL (FIGURE 3)		
Line and description	Radius, cm.	d(Å.)
1 Dark region in center	0.64	7.33
2 Broad and intense	1.05	4.58
3 Distinct	1.275	3.84
4 Faint	1.56	3.24
5 Faint	1.865	2.80
6 Faint	2.24	2.44
7 Intense	2.55	2.22

POLYVINYL ACETATE (FIGURE 4)		
Line and description	Radius, cm.	d(Å.)
1 Intense	0.7	6.74
2 Intense	1.24	3.95
3 Hazy	2.7	2.15

### Summary

1. It has been found that polyvinyl alcohol is not oxidized by periodic acid and hence does not contain 1,2-glycol units.

2. Chromic acid oxidation of polyvinyl alcohol followed by alkaline hydrolysis has been found to produce acetone and acetic acid, which is definite evidence for the 1,3-glycol structure in polyvinyl alcohol.

3. The ultraviolet absorption of polyvinyl alcohol has been shown to be similar to that of 2,4-pentanediol.



4. X-ray patterns of polyvinyl alcohol and polyvinyl acetate have been described.

5. Some reactions of polyvinyl alcohol with

boric acid, ethyl oxalate, and bromine water have been investigated.

URBANA, ILLINOIS

RECEIVED FEBRUARY 23, 1938

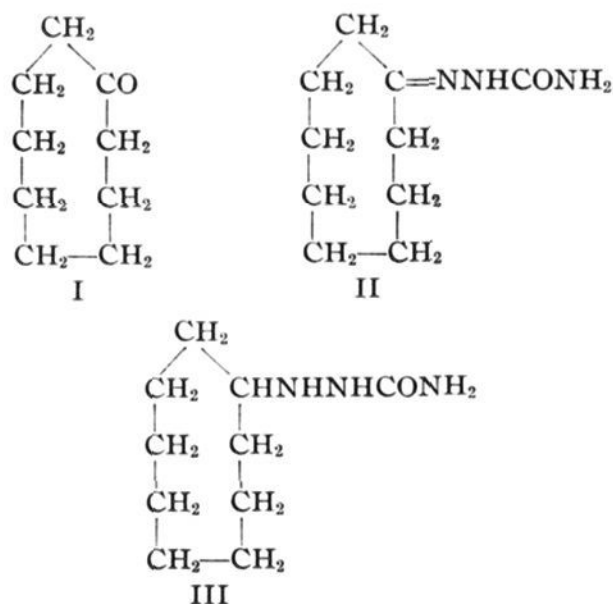
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

## The Possible Asymmetry of a Monosubstituted Cyclononane<sup>1</sup>

BY C. S. MARVEL AND DUDLEY B. GLASS

Construction of a model of a monosubstituted cyclononane using the atomic models developed by Stuart<sup>2</sup> has shown that two arrangements of the atoms are possible and that one of these models is a non-superimposable mirror image of the other (Fig. 1). Consequently it has seemed worth while to prepare a monosubstituted cyclononane and attempt its resolution.

Cyclononanone (I) was prepared from the thorium salt of sebacic acid by the procedure of Ruzicka and Brugger.<sup>3</sup> It was then converted to the semicarbazone (II) for final purification and the pure semicarbazone was reduced to 1-cyclononylsemicarbazide (III).



The salts of this base with Reychler's *d*-camphor-sulfonic acid and with *d*- $\alpha$ -bromocamphor- $\pi$ -sulfonic acid were prepared and submitted to fractional crystallization. No evidence of resolution was obtained.

Our experiments on this cyclononane derivative furnish evidence that these rigid models of mole-

(1) The concept that a monosubstituted cyclononane might exist in two optically active forms arose during a discussion between the late W. H. Carothers, J. B. Conant, B. S. Garvey, John R. Johnson and one of the authors on the evening of December 31, 1935, during the sixth National Organic Chemistry Symposium at Rochester, N. Y.—C. S. M.

(2) Stuart, *Z. physik. Chem.*, **B27**, 350 (1934).

(3) Ruzicka and Brugger, *Helv. Chim. Acta*, **9**, 389 (1926).

cules do not present a true picture of the flexibility of the molecules themselves. It is of interest to note that the cyclohexane molecule constructed from the Stuart atomic models cannot be easily shifted from the "boat" to the "chair" form. This shift must actually occur easily in the cyclohexane molecule.<sup>4</sup>

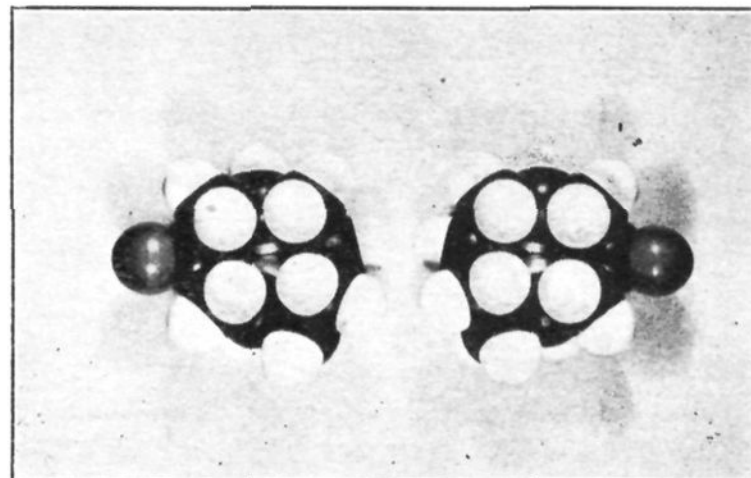


Fig. 1.

In connection with this work some new derivatives of cyclooctane have been prepared in order to develop methods of procedure with these homologs before carrying out reactions with the difficultly obtainable cyclononane derivatives.

### Experimental

Cyclooctanone semicarbazone, m. p. 168–169°, was prepared from thorium azelate by the method of Ruzicka and Brugger.<sup>5</sup>

*Anal.* Calcd. for C<sub>9</sub>H<sub>17</sub>ON<sub>3</sub>: N, 22.95. Found: N, 22.99.

Cyclononanone semicarbazone, m. p. 178–179°, was obtained in a similar manner from thorium sebacate. Ruzicka and Brugger<sup>3</sup> report that this compound melts at 178° and Ziegler and Aurnhammer<sup>6</sup> report the melting point as 184°. An analysis of our product indicated that it was very pure.

(4) Professor W. H. Mills first pointed out this weakness of the Stuart models to us. He also predicted that the resolution of a monosubstituted cyclononane would not be accomplished.

(5) Ruzicka and Brugger, *Helv. Chim. Acta*, **9**, 339 (1926).

(6) Ziegler and Aurnhammer, *Ann.*, **513**, 43 (1934).