TABLE II

STOICHIOMETRIC CARBOXYLATION OF PROPARGYL ALCOHOL WITH NICKEL CARBONYL. EFFECT OF ESTERIFICATION VARIABLES

Expt. no.	H_2SO_4 catalyst (ml.)	Reflux rate (ml./min.)	Reaction time (hr.)	Yield of esters III (%)	IV (%)
1	2	4	3	33	7
2	5	12	11	50	8
3	10	4	23	48	8
4	5	4	3	39	5
5	2	12	11	48	10
6	5	4	7	50	7
7	2	4	11	50	9
8	2	12	3	45	5
9	5	12	7	52	6
10	2	4	7	41	8
11	5	12	3	37	8
12	5	4	11	49	7
13	2	12	7	36	8
14[a]	5	12	24	44	2
15[a]	10	12	24	51	10

[a] In these experiments, no attempt was made to remove the water formed during the reaction.

nickel carbonyl) into a 2-l. round-bottom flask. Concentrated sulfuric acid (5 ml.) was added, and the solution was refluxed for at least 7 hr. through a Soxhlet extractor containing anhydrous magnesium sulfate. The reaction mixture was cooled, and sodium hydroxide (53 ml., 5 *N*) was added to neutralize the catalyst. The mixture was then distilled under reduced pressure until the bumping became excessive. At this point twice the volume of water was added, and the solution was extracted with three 200-ml. portions of chloroform. The chloroform was distilled and the residue fractionally distilled at reduced pressure through a 6-in. Vigreux column. There were obtained 158 g. (58% yield) of IV, b.p. 65–70° (1 mm.), n^{20}D 1.4480, and 29 g. (11% yield) of V, b.p. 85–90° (1 mm.), n^{20}D 1.4590.

Anal. Calcd. for $C_6H_{10}O_3$ (IV): hydrogen no., 1.0; sapon. equiv., 130; mol. wt., 130. Found: hydrogen no., 1.09; sapon. equiv., 129; mol. wt. (b.p. elevation), 133.

Compound V was characterized by conversion to its *p*-nitrobenzoate, m.p. 75–76°. Compound V also was saponified to *trans*-γ-hydroxycrotonic acid, m.p. 104–105°, lit.[8] m.p. 108.

When the carboxylation was carried out in benzene and in absolute ethanol, the yields of IV were 51 and 48%, respectively. When the carboxylation was carried out by adding the nickel carbonyl last, the yield of IV was 23%, and when both nickel carbonyl and propargyl alcohol were added simultaneously, the yield was 41%. When the molar ratio of propargyl alcohol to acetic acid was changed to 2:1 and 1:2, the yields of IV were 41 and 49%, respectively.

When methyl alcohol, isobutyl alcohol, and *n*-butyl alcohol were used as solvents for the carboxylations and esterifications, there were obtained, respectively, II, b.p. 62–70° (1 mm.), n^{25}D 1.4490; isobutyl α-(hydroxymethyl)acrylate, b.p. 70–75° (1 mm.), n^{26}D 1.4375; and *n*-butyl α-(hydroxymethyl)acrylate, b.p. 72–75° (0.3 mm.), n^{25}D 1.4412, in 50, 56, and 25% yields, respectively.

The Effect of Variables in the Esterification on the Yields of IV and V.—A 16-mole carboxylation of propargyl alcohol in ethanol was performed as described in the preceeding section, and the resulting carboxylation solution was freed of nickel and esterified in 1-mole quantities in a set of experiments statistically designed to study the effect of the quantity of sulfuric acid catalyst, the reflux rate, and the reaction time. The results, given in Table II are evaluated in the discussion part of this paper.

Catalytic Carboxylation of Propargyl Alcohol to Ethyl α-(Hydroxymethyl)acrylate (IV) and Ethyl *trans*-γ-Hydroxycrotonate (V).—A 1-gal. stirring autoclave was charged with 95% ethanol (572 ml.), acetic acid (120 g., 2 moles), propargyl alcohol (112 g., 2 moles), water (8 ml.), and hydroquinone (0.1 g.). After being purged with nitrogen and carbon monoxide, the autoclave was heated to 125° and maintained under 200 p.s.i.g. of carbon monoxide. A solution of nickel carbonyl (15.4 g., 0.09 mole) in absolute ethanol (120 ml.) was fed under pressure from a Jerguson gage to the autoclave in 60 min. The carbon monoxide absorption, as measured from a calibrated reservoir, was 160 p.s.i.g. (2 moles). The reaction mixture was cooled to room temperature, the gases vented to the atmosphere, and the contents removed. At this point, the crude product was treated in a manner similar to that used for the carboxylations with stoichiometric quantities of nickel carbonyl. There were obtained 150 g. (58% yield) of IV and 20 g. (11% yield) of V.

A series of nickel carbonyl-catalyzed carboxylations was carried out in which the variables of temperature, pressure, molar ratio of reactants, and order of addition of reactants were studied. The results are presented in the discussion part of this paper.

Acknowledgment.—The authors are indebted to Drs. W. M. Kutz and A. J. Kolka for their help in discussing this work, and to the Chemical and Instrumental Analysis Laboratory Group of the Koppers Company, Mrs. Jean W. Biss and Mr. James P. Davis, for some of the analyses conducted in connection with this work.

Starch Acetals. I. Reaction of Starch with 3,4-Dihydro-2*H*-pyran[1]

OLLIDENE WEAVER, C. R. RUSSELL, AND C. E. RIST

Northern Regional Research Laboratory,[2] Peoria, Illinois

Received July 16, 1962

Starch acetals were prepared by a method which does not generate water or form cross links. The acetals were made by treating starch with the cyclic vinyl ether, 3,4-dihydro-2*H*-pyran, whose concentration largely determined the average degree of substitution. The products were soluble in water at lowest levels of substitution (0.03 to 0.15) and insoluble at intermediate levels (0.2 to 0.45). When the degree of substitution reached 0.7, 1.1, and 1.5, the acetals became soluble in dioxane, chloroform, and benzene, respectively.

Studies were initiated on the preparation of starch acetals without generating water or forming cross links. This objective was desirable because water is removed with much difficulty from hydrophilic polymers and intermolecular cross links in starch rapidly lead to insoluble products.

Acetals are most commonly prepared by reaction of aldehydes with alcohols in the presence of an acid catalyst. Although treatment of starch with formaldehyde to obtain products with specific properties has long been used commercially, the mechanism of the action of aldehydes on starch is probably complex and not well

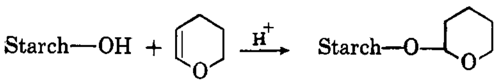
---

(1) Presented before the Division of Carbohydrate Chemistry, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962.

(2) This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

understood. Hiemstra, Muetgeert, and Bus[3] view it as a two-step reaction. The first step takes place in aqueous solution leading to formation of hemiacetals in equilibrium with the reaction components, and the second step, during which a full acetal is formed, occurs when the hemiacetals are cured at 130° in the presence of an acid catalyst. Cross-linked, more or less insoluble, polymers are obtained.

Acetals in this study were prepared by the alternative method of adding an alcohol to the double bond of a vinyl ether.[4,5] This reaction, not previously reported with starch, minimizes the possibility of cross-linking and forms no water in the course of the reaction. The present paper reports the preparation and properties of starch acetals ranging in average degree of substitution (D.S.) from 0.03 to 2.6 made by treating starch with the cyclic vinyl ether, 3,4-dihydro-2*H*-pyran.



As anticipated, little or no cross linking occurred, presumably because of the stability of the six-membered ring.

Results and Discussion

By treating granular starch with dihydropyran in the presence of an acid catalyst, products were obtained having an average degree of substitution no greater than 0.03, but by using dimethyl sulfoxide as a starch solvent products having average degree of substitution up to 2.6 were obtained. The reaction temperature did not appear to be critical up to 56°—above this, coloration occurred. Color also appeared in reaction mixtures in which starch was omitted, suggesting a side reaction of the dihydropyran. An acid catalyst is required and 0.027 mole of hydrogen chloride per 162 g. of starch gave satisfactory catalysts.

Products were made ranging in average degree of substitution from 0.03 to 2.6. For the most part, the average degree of substitution was controlled by the amount of dihydropyran used. The results from a series of reactions in which varying molar ratios of dihydropyran to starch were employed are given in Table I. The reaction conditions were those of the general procedure given in the Experimental section. A ratio of 1.6 moles of dihydropyran per 162 g. of starch was most efficient, giving an average degree of substitution of about 1. Increasing the molar ratio of dihydropyran to starch above about 5 did not increase the average degree of substitution beyond 2.10 unless the amount of dimethyl sulfoxide and reaction time also were increased.

In general, the reaction proceeded rapidly for the first half hour with a gradual decrease thereafter. A three-hour reaction time was chosen because shorter periods gave less reproducible results, and longer periods were not practical. In an altered reaction procedure using double the usual solvent volume, with 11.6 moles of dihydropyran/162 g. of starch, the degree of substitution was 2.2 after three hours and 2.5 after forty-eight hours.

TABLE I

EFFECT OF DIHYDROPYRAN CONCENTRATION ON DEGREE OF SUBSTITUTION

Moles of dihydropyran/162 g. of starch	Yield,[a] %	Degree of substitution[b]	Analysis, % C	Analysis, % H
0	...	0	44.53	6.21
0.4	143.5	0.15	46.58	6.62
0.8	161.3	0.39	48.85	6.93
1.6	216.2	1.10	54.42	7.50
3.2	293.6	1.75	57.29	7.84
4.8	323.1	2.10	58.51	7.97
6.4	327.6	2.10	58.58	8.14
11.6[c]	332.0	2.50	59.46	8.06

[a] Expressed in grams per 162 g. of starch. [b] Degree of substitution calculated from carbon values. [c] Procedure altered by doubling the amount of solvent and extending the reaction time to 48 hr.

TABLE II

EFFECT OF MOISTURE ON DEGREE OF SUBSTITUTION

Moisture, %	Moles of dihydropyran/162 g. of starch	Degree of substitution
3.0	0.4	0.05
0.3	0.4	0.15
3.0	0.8	0.26
0.3	0.8	0.39
3.0	1.6	0.40
0.3	1.6	1.10

Drying the starch to a moisture content of less than 1% resulted in higher degree of substitution than was obtained with starch of 3% moisture (Table II). Since the reduction in degree of substitution at higher moisture levels is greater than can be acounted for by the loss of dihydropyran through hydrolysis, it may be assumed that water inhibits the reaction.

After isolation, the products were tested for solubility in a number of representative solvents. A sample was defined as being soluble if 0.2 g., when stirred with 1 ml. of solvent, gave a clear gel and, upon dilution with an additional 15 ml. of the solvent, gave a clear solution. Products in the degree of substitution range of 0.03 to 0.15 were soluble in water. At or above degree of substitution values of 0.7, 1.1, and 1.5, the acetals were soluble in dioxane, chloroform, and benzene, respectively. The high yield of soluble products obtained indicate that retention of the six-membered ring is favored over formation of cross links *via* alcohol interchange.

No study of the molecular size of the products has been made; however, intrinsic viscosities, as shown in Table III, indicate the molecular weight of the starch acetals is considerably less than that of the unmodified starch.

TABLE III

Degree of substitution	$[\eta]^{1N}{}_{KOH}$	$[\eta]_{DMSO}$	$[\eta]_{benzene}$
0	1.40	1.48	
0.05	0.84	0.85	
0.15	1.05		
0.95		0.82	
1.58		0.42	0.31
2.1			0.46
2.6			0.49

---

[3] Von P. Hiemstra, J. M. Muetgeert, and W. C. Bus, *Die Stärke*, (9) **10**, 213 (1958).

[4] R. E. Kirk and D. F. Othmer, "Encyclopedia of Chemical Technology," Vol. 11., The Interscience Encyclopedia, Inc., New York, N. Y., 1953, pp. 652,653.

[5] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., and Chapman and Hall, Ltd., London, 1953, p. 266.

Carbon analyses of low degree of substitution (0.03–0.05) products did not show conclusively that reaction had occurred; however, the products dispersed in hot water more readily than the control starch. Also, following hydrolysis of the acetal in dilute acid, some of the expected 5-hydroxypentanal was obtained in the form of the 2,4-dinitrophenylhydrazone. This derivative could not be used as a measure of the degree of substitution because it was impossible to separate the hydroxypentanal quantitatively from the hydrolysis mixture.

Experimental

Materials.—Edible grade commercial wheat starch was dried in a forced-air oven at 100° for 1 hr. to a moisture content of about 3%, and at 110° (with frequent mixing) for 2 hr. to a moisture content of 0.3 to 1%. Eastman[6] practical grade 3,4-dihydro-2*H*-pyran (n^{25}_{D} 1.4372, lit.[7] n^{19}_{D} 1.4402) was used without further purification. Reagent grade dimethyl sulfoxide as obtained from J. T. Baker was sufficiently anhydrous for the reaction. The catalyst was prepared by bubbling hydrogen chloride into 1,4-dioxane, and its concentration determined by titrating with standard base.

Intrinsic Viscosity.—Intrinsic viscosities were determined at 25° with Ostwald-Cannon-Fenske no. 100 viscometers. Samples were dispersed in 1 *N* potassium hydroxide, dimethyl sulfoxide, or benzene depending on the solubility of the sample involved.

Preparation of Starch Acetals. General Procedure for Degree of Substitution Range 0.3 to 2.2.—A typical preparation with dispersing agent was carried out as follows. Starch (10 g., 0.062 mole) with less than 1% moisture was gelatinized with 100 ml. of dimethyl sulfoxide by mechanical stirring and heating on a steam bath for 0.5 hr. The mixture was then cooled to 50° and maintained at this temperature throughout the reaction. One-fourth milliliter of a solution of 25% hydrochloric acid in dioxane was added, thereafter 18 ml. (0.20 mole) of 3,4-dihydro-2*H*-pyran (DHP) was added dropwise over a period of 15–20 min. Stirring was continued for 3 hr. Then the clear, viscous, reaction mixture was poured into excess water (*ca.* 300–400 ml.). The clumps of product were broken up by stirring in a Waring Blendor. The white solid was isolated on a fritted-glass funnel and washed thoroughly with three 200-ml. portions of water. The solid product was spread in a thin layer and allowed to air-dry overnight. It was then dried in a forced-air oven at 100° for 1 hr., weight, 18.2 g. The product was ground through a 40-mesh screen in a Wiley mill. A sample was further dried under vacuum at 100° for 2 hr. and analyzed for carbon and hydrogen.

Anal. Calcd. for D.S. 1.75: C, 57.27; H, 7.82. Found: C, 57.15; H, 7.86.

This product was soluble in dioxane, chloroform, benzene, and difficultly soluble in dimethyl sulfoxide. Ten grams of product formed a very viscous solution in 100 ml. of benzene and was precipitated by the addition of excess petroleum ether. Weight on drying was 9.5 g. This material after milling and drying as described gave the following analysis: C, 57.43; H, 7.82.

Procedure for Degree of Substitution above 2.2.—For highest degree of substitution certain alterations in the general procedure had to be made. For example 5 g. (0.03 mole) of starch of less than 1% moisture was gelatinized with 125 ml. of dimethyl sulfoxide by mechanical stirring and heating on a steam bath for 0.5 hr. The reaction flask was then placed in a constant temperature bath (45–48°) and 0.25 ml. of 25% hydrochloric acid in dioxane was added to the reaction mixture. Thereafter, 32 ml. (0.35 mole) of 3,4-dihydro-2*H*-pyran was added dropwise. After continued stirring for 48 hr., the product was precipitated by pouring into water and worked up as in the general procedure, weight, 10.1 g. The product was soluble in dioxane, chloroform, and benzene.

Anal. Calcd. for D.S. 2.60: C, 59.93; H, 8.10. Found: C, 59.83, 59.84; H, 8.02, 8.02. After dissolving in benzene and reprecipitating with petroleum ether, the analysis was: C, 59.53, 59.39; H, 8.11, 8.01.

Procedure for Degree of Substitution Range 0.05 to 0.15.—For low degree of substitution the general procedure was followed, except that absolute ethanol was substituted for water as a precipitating agent. For example, 10 g. (0.062 mole) of starch of less than 1% moisture, 100 ml. of dimethyl sulfoxide 0.25 ml. of 25% hydrochloric acid in dioxane, and 2.2 ml. (0.024 mole) of 3,4-dihydro-2*H*-pyran were treated as described. After the 3-hr. period of stirring, the reaction mixture was poured into excess absolute ethanol, stirred, and isolated by filtration. The gummy mass which formed on drying was dissolved in a small amount of water with the aid of a Blendor and precipitated by pouring into excess 95% alcohol. The precipitate was washed thoroughly with 95% alcohol, dried, and milled; weight, 9 g.

Anal. Calcd. for D.S. 0.15; C, 46.41, H, 6.41. Found: C, 46.65, 46.52; H, 6.60, 6.62.

This product was water soluble and foamed readily with shaking in dilute solution.

No Dispersing Agent.—Seventy grams (0.43 mole) of starch was placed in a steel beaker and stirred while a mixture of 15 ml. (0.17 mole) of 3,4-dihydro-2*H*-pyran and 1 ml. of 20% hydrochloric acid in dioxane was added dropwise. The mixture was stirred for 3 hr. after which 100 ml. of benzene was added with thorough mixing. The solid was isolated by filtration, washed thoroughly with benzene, and dried in a forced-air oven; weight, 72 g.

Anal. Found: C, 44.56; H, 6.38.

After gelatinizing in water, a dilute solution gives a stable foam. A 2,4-dinitrophenylhydrazone derivative of 5-hydroxypentanal was obtained after hydrolyzing with 10% sulfuric acid and steam distilling into a 2,4-dinitrophenylhydrazine solution until no more precipitate formed.

The 2,4-dinitrophenylhydrazone of 5-hydroxypentanal was recrystallized from aqueous alcohol, m.p. 109° (lit.[8] m.p. 107–109°).

Anal. Calcd: C, 46.81; H, 4.96; N, 19.85. Found: C, 46.54; H, 4.75; N, 19.44.

Acknowledgement.—The authors wish to thank James L. Minor for a number of laboratory preparations and Bonita R. Heaton, Kay A. Horton, Elizabeth R. Matushek, and Clara E. McGrew for the microanalyses.

---

(6) The mention of firm names or trade products does not imply that they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

(7) R. Paul, *Bull. soc. chim.*, **53**, 1489 (1933).

(8) G. F. Woods and D. N. Kramer, *J. Am. Chem. Soc.*, **69**, 2246 (1947).