5,5′-Ethylenedioxybis(5*H*-dibenz[*c,e*]azepine) (XI).—Cupric acetate monohydrate (7.5 g., 0.038 mole) was added to a solution of II (15 g., 0.072 mole) in ethylene glycol (150 ml.) and water (30 ml.) and the mixture refluxed for 1.5 hr. Precipitated cupric hydroxide was removed by filtration and chloroform added to the filtrate. The chloroform was washed with 7% aqueous sodium bicarbonate (300 ml.) and then with water. After separation, the chloroform layer was evaporated to a volume of 200 ml., and *n*-heptane was added to cause crystallization of the crude product (11.7 g., 71%), m.p. 227–232°. Recrystallization from chloroform–acetone gave the pure compound, m.p. 244–246°.

Anal. Calcd. for $C_{30}H_{24}N_2O_2$: C, 80.96; H, 5.44; N, 6.30. Found: C, 80.79; H, 5.58; N, 6.26.

2,2′-Bis(1-hydroxy-2-benzoylethyl)biphenyl (XII).—A solution of sodium hydroxide (2.1 g.) in water (80 ml.) was added to a solution of I (4.6 g., 0.022 mole) in ethanol (80 ml.). Acetophenone (5.2 g., 0.044 mole) was added to the resulting solution over a 1-min. period. Colorless crystals soon formed and after only several minutes were collected, washed with ethanol (−5 to 0°), and dried. This yielded 5.5 g. (55%) of crude XII, m.p. 175–185°. Recrystallization from methanol gave the pure compound, m.p. 238.5–239.0° dec.

Anal. Calcd. for $C_{30}H_{26}O_4$: C, 79.75; H, 5.81. Found: C, 79.74; H, 5.69.

The use of one molar equivalent of acetophenoneas before gave 35% yield of XII and 57% yield of diphenide, m.p. 124–130° (lit.[3,4] m.p. 132°). The infrared spectrum was identical with that of authentic diphenide.

2-Diacetoxymethyl-2′-(benzoylvinylene)biphenyl (XIII).—Six grams of XII was refluxed in acetic anhydride (100 ml.) for 1 hr. The acetic anhydride was removed by flash evaporation. The residual oil was dissolved in ethanol, from which, on concentration, 3.9 g. (70%) of crude XIII, m.p. 197–204°, was obtained. Recrystallization from ethyl acetate gave the pure compound, m.p. 208.5–209.5°.

Anal. Calcd. for $C_{28}H_{22}O_5$: C, 75.30; H, 5.36. Found: C, 74.92; H, 5.46.

2,2′-Bis(hydroxymethyl)biphenyl (XIV). Method A.—Aluminum isopropoxide (2.8 g., 0.014 mole) was mixed with anhydrous isopropyl alcohol (100 ml.) containing I (4.2 g., 0.02 mole). Acetone was distilled from the reaction through a 12-in. Vigreux column followed by the majority of the isopropyl alcohol. The cooled reaction mixture was poured into 20% hydrochloric acid (100 ml.). The precipitated 2,2′-bis(hydroxymethyl)biphenyl (4.01 g.), m.p. 92–100°, was collected, washed, and dried. Recrystallization from benzene gave 2.79 g. (65%) of material melting at 109.4–109.8° (lit.[15] m.p. 112–113°).

Method B.—Compound I (15 g.) in ethanol (100 ml.) was hydrogenated (50 p.s.i.) over Raney nickel catalyst (0.5 g.) at 52° for 18 hr. After removal of the catalyst by filtration, the ethanol was flash evaporated and the residue recrystallized from benzene to give 12.4 g. (81%) of XIV, m.p. 109.0–109.8°.

9,10-Phenanthraquinone (XV).—A solution of I (2.1 g., 0.01 mole) in acetone (100 ml.) containing benzoyl peroxide (0.02 g.) was refluxed for 7 hr. with continuous irradiation from a mercury vapor lamp (Hanovia Chemical and Manufacturing Co., type 16200; filter removed) at a distance of 5–6 in. The solution was aerated at the rate of approximately 0.06 S.C.F.M. The acetone was flash evaporated, and a 50% yield of 9,10-phenanthraquinone, m.p. 196–206° (lit.[22] m.p. 206–207°), was recovered by washing residue with ethyl ether. The material dissolved in the ether was largely unchanged dialdehyde, identified by an infrared spectrum.

Other solvents—*t*-butyl alcohol, acetic acid, benzene, ethyl ether, tetrahydrofuran, and xylene—were employed similarly, except that the reaction time was 48 hr. at room temperature followed by 3 hr. at reflux.

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Carboxylation of Propargyl Alcohol

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The carboxylation of propargyl alcohol with stoichiometric quantities of nickel carbonyl and with carbon monoxide in the presence of catalytic amounts of nickel carbonyl has been accomplished. Carboxylation of propargyl alcohol in ethyl alcohol at 55° with stoichiometric quantities of nickel carbonyl followed by esterification of the resulting products gave a 58% yield of ethyl α-(hydroxymethyl)acrylate (IV) and, surprisingly, an 11% yield of ethyl *trans*-γ-hydroxycrotonate (V). In general, the addition of the elements of formic acid ($H-CO_2H$) to a terminal acetylene group is expected to give a product of the type of IV. This is the first time that a substantial amount of the reversed addition product V has been isolated. When the sequence of reactions was carried out in methyl, isobutyl, and *n*-butyl alcohols, the corresponding esters were obtained. The carboxylation of propargyl alcohol was also accomplished for the first time with carbon monoxide in the presence of catalytic quantities of nickel carbonyl. The yields of IV and V were equal to those obtained in the stoichiometric reaction. In the catalytic carboxylation it was found that for a given temperature, over the range studied, there was a corresponding maximum pressure above which no reaction occurred.

Jones, Shen, and Whiting[4] reported that an exotherm was observed when nickel carbonyl was added to a solution containing propargyl alcohol and acetic acid, but they were not able to isolate any identifiable product. When we carried out the reaction by adding the propargyl alcohol to the other reactants, an 18% yield of α-(hydroxymethyl)acrylic acid (I) was obtained. An

$$4H\text{-}C{\equiv}C\text{—}CH_2OH + Ni(CO)_4 + 4H_2O + 2CH_3CO_2H \xrightarrow[C_2H_5OH]{55°} \underset{\text{I}}{4CH_2{=}C(CH_2OH)\text{—}COOH} + Ni(CH_3CO_2)_2 + 2[H] \quad (1)$$

analysis of the crude carboxylation product was then undertaken to find the reason for the low yield of acid isolated. Quantitative hydrogenation of the product indicated a higher degree of unsaturation than was shown by bromination. An increase in acid content after hydrogenation suggested that an ester initially present had undergone hydrogenolysis. When the crude product was freed of nickel and treated with diazomethane, esters were obtained which were analyzed by vapor phase chromatography. It was found that the esterified product consisted of 2.4% methyl meth-

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[4] E. R. H. Jones, T. Y. Shen, and M. C. Whiting, *J. Chem. Soc.*, 230 (1950).

acrylate, 34% methyl α-(hydroxymethyl)acrylate (II), and 42% methyl α-(acetoxymethyl)acrylate as well as unidentifiable products. These results indicated that the crude carboxylation product contained both I and α-(acetoxymethyl)acrylic acid (III) and explained the low yield of I obtained by direct distillation. It was then decided to direct efforts toward isolation of the esters of I. Jones, *et al.*,[4] studied the action of methanol and sulfuric acid on III and reported an undisclosed yield of a compound which they claimed was II without giving any details of characterization. We synthesized III in 30% yield by the carboxylation of propargyl acetate with nickel carbonyl[5] and then caused it to react as shown in equation 2 with ethanol, in the presence of sulfuric acid, to give an 82% yield of ethyl α-(hydroxymethyl)acrylate (IV).

$$\underset{\text{III}}{H_2C{=}C(CH_2OCOCH_3){-}COOH} + 2C_2H_5OH \xrightarrow{H_2SO_4}$$

$$\underset{\text{IV}}{H_2C{=}C(CH_2OH)CO_2C_2H_5} + CH_3CO_2C_2H_5 \qquad (2)$$

Compound IV was characterized by analysis for unsaturation (mercuric acetate nonaqueous titration),[6] infrared spectrum, and saponification equivalent. Its physical constants agreed with those reported by Ferris[7] for IV. Our method of product isolation, which should convert both I and its acetate to the same ester, was then tried on a crude carboxylation solution. After the ionic nickel was precipitated as nickel sulfate hexahydrate with 50% sulfuric acid, concentrated sulfuric acid was then added to the filtrate, and the solution was refluxed for twenty-four hours. A 58% yield of IV and, surprisingly, an 11% yield of ethyl *trans*-γ-hydroxycrotonate (V), were obtained.

$$\underset{\text{V}}{HOCH_2CH{=}CH{-}CO_2C_2H_5}$$

Compound V was characterized by conversion to the *p*-nitrobenzoate[8] and to the free acid.[8] In general, the addition of the elements of formic acid ($H{-}CO_2H$) to a terminal acetylene group obeys the Markovnikov's rule.[9] Isolation of V by us is the first time that a substantial amount of the reversed addition product has been obtained.

In the carboxylation of propargyl alcohol with stoichiometric amounts of nickel carbonyl, the best results were obtained by addition of propargyl alcohol to the other reagents, by use of 95% ethyl alcohol as solvent, and by use of 1:1 ratio of propargyl alcohol to acetic acid. This latter value was unexpected, since equation 1 indicates a 2:1 ratio. The esterification step then was studied to find the optimum conditions. In a statistically designed set of experiments (Table II) it was found that, if the esterification was carried out so that water was removed as formed, the optimum yield (about 55%) of IV could be obtained by refluxing one mole of acid for seven hours in the presence of 5 ml. of concentrated sulfuric acid or for eleven hours in the presence of 2 ml. of sulfuric acid. If no attempt was made to remove the water formed, the same yield was obtained by twenty-four-hour reflux in the presence of 10 ml. of sulfuric acid. This sequence of reactions was applicable to preparation of other esters of I. Propargyl alcohol was carboxylated and then esterified in methyl, isobutyl, and *n*-butyl alcohols, and the major products obtained were II, isobutyl α-(hydroxymethyl)-acrylate, and *n*-butyl α-(hydroxymethyl)acrylate in 50, 56, and 25% yields, respectively.

The success of the carboxylation of propargyl alcohol with stoichiometric quantities of nickel carbonyl led us to investigate carboxylation with carbon monoxide in the presence of catalytic quantities of nickel carbonyl. In a preliminary experiment at 2000 p.s.i. it was found that no gas absorption occurred when an attempt was made (analogous to the semicatalytic carboxylation of acetylene[10]) to superimpose the catalytic reaction 3 on the stoichiometric reaction 1.

$$H{-}C{\equiv}C{-}CH_2OH + CO + H_2O \longrightarrow CH_2{=}C{-}(CH_2OH){-}COOH \qquad (3)$$

Further experiments then showed (Table I) that, for each temperature in the reaction range studied, there was a maximum pressure above which there was a marked reduction in rate of carbon monoxide absorption. At pressures approximately 10% higher than the maximum, the carbon monoxide absorption rate was essentially zero.

TABLE I

CATALYTIC CARBOXYLATION OF PROPARGYL ALCOHOL WITH CARBON MONOXIDE IN THE PRESENCE OF NICKEL CARBONYL. REACTION TEMPERATURE *vs.* MAXIMUM PRESSURE

Temperature (°C.)	Maximum CO pressure (p.s.i.g.)
85	20
90	25
105	65
115	90
120	95
127	200
135	210
140	240
145	550

Some reaction variables were studied and the following effects were noted.

1. **Effect of Pressure at Constant Temperature.**—It was found that when the reaction was carried out at 127°, the yield of IV reached a maximum near the maximum workable pressure for that temperature. At carbon monoxide pressures of 125, 150, 175, 200, and 225 p.s.i.g., the respective yields of IV were 32, 43, 48, 53, and 0%.

2. **Effect of Temperature.**—Variation in yield of IV (50–55%) over the temperature range of 85–145° was not significant as long as the reaction was carried out at the maximum operable pressure for that temperature.

3. **Effect of Propargyl Alcohol–Nickel Carbonyl Ratio.**—It was found that, within experimental error, the same yield of IV was obtained when 0.030–0.076 mole of nickel carbonyl was used per mole of propargyl alcohol, but the time required for maximum absorption of carbon monoxide was shortest at 0.053 mole. For

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[7] A. F. Ferris, *J. Org. Chem.*, **20**, 784 (1955).

[8] R. Rambaud, *Compt. rend.*, **220**, 742 (1945).

[9] E. R. H. Jones, T. Y. Shen, and M. C. Whiting, *J. Chem. Soc.*, 48 (1951).

[10] H. T. Neher, E. H. Specht, and A. Neuman, U. S. Patent 2,582,911.

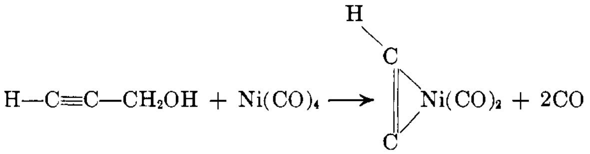
a one-mole experiment this reaction time was in the range of one hour.

4. Order of Addition of Reactants.—The order of addition of reactants did not affect the yield of IV. Control of exotherm and minimum usage of nickel carbonyl were most easily effected by addition of the nickel carbonyl to the other reactants. These results differed from those obtained in the carboxylation of propargyl alcohol with stoichiometric quantities of nickel carbonyl where addition of the propargyl alcohol to the other reactants gave the best yields of IV.

The mechanism of the carboxylation reaction is not known, although workers in the field have made pertinent and valuable observations in the past. Originally, Reppe[11] postulated a cyclopropenone intermediate, but recent work by Bird and Hudec,[12] in which they recovered diphenylcyclopropenone unchanged after treatment with hydrochloric acid in ethanol–benzene, indicates that this mechanism is not valid. Jones, *et al.*,[13] investigated the quantitative aspects of the reaction by varying the ratio of the reactants and came to the conclusion that, since the yields were always about 50%, two moles of acetylene gave rise to one mole of the product. The results of their study were summarized in the following equation.

$$10\text{R—C}\equiv\text{C—R}' + 2\text{Ni(CO)}_4 + 5\text{H}_2\text{O} + 4\text{HX} \longrightarrow 5\text{RC(CO}_2\text{H)}=\text{CHR}' + 2\text{NiX}_2 + (5\text{RC}\equiv\text{C—R}'\ 3\text{CO},\ 4\text{H})$$

The last term represents net composition of a complex mixture of by-products. In carboxylations of propargyl alcohol the combined yield of acrylate and crotonate esters isolated was about 65%, and thus proposed stoichiometry cannot be considered applicable. In view of our finding that for each workable temperature there is a pressure of carbon monoxide above which no reaction occurs, it seems likely that the first step involves the formation of a complex which is accompanied by the evolution of carbon monoxide.



In support of such a postulated step are the facts that acetylene and cobalt carbonyl have been shown by Wender, *et al.*,[14] to form an analogous compound with the evolution of carbon monoxide and that in the hydroformylation reaction carbon monoxide is evolved in the first step and excessive carbon monoxide pressure inhibits the reaction.[15–17]

Experimental[18]

Carboxylation of Propargyl Alcohol to α-(Hydroxymethyl)-acrylic Acid (I).—Into a 1-l. round-bottom flask equipped with a stirrer, thermometer, Dry Ice-cooled condenser, and dropping funnel were placed acetic acid (60 g., 1 mole), nickel carbonyl (53 g., 0.31 mole), water (20 g., 1.1 moles), ethanol (200 ml.), and hydroquinone (0.1 g.). The solution was refluxed (40°) and propargyl alcohol (56 g., 1 mole) was added dropwise over 1 hr. The reaction was exothermic and the temperature was controlled by the rate of addition of propargyl alcohol. The temperature rose gradually to 86° during the addition. The mixture was stirred for another hour, treated with 10% sodium hydroxide (500 ml.), and the precipitated nickel oxide removed by filtration. The filtrate was acidified to pH 2.5 with hydrochloric acid and the solution flash-distilled to a pot tempersure of 100° at 25 mm. The residue was extracted with five 100-ml. portions of ethanol, the ethanol removed, and the residue distilled at 1 μ and 90–100° (bath temperature) to give 15 g. (18% yield) of α-(hydroxymethyl)acrylic acid (I).

Anal. Calcd. for $C_4H_6O_3$: C, 47.1; H, 5.96; acid no., 102. Found: C, 47.6; H, 6.08; acid no., 107.

The *p*-bromophenacyl ester melted at 67.5–68°.

Reaction of I with cuprous chloride and hydrochloric acid at room temperature for 6 hr. gave α-(chloromethyl)acrylic acid, m.p. 58.5–59.° (petroleum ether), lit.[19] m.p. 62–64°.

Analyses of Carboxylation Product.—Propargyl alcohol (28 g., 0.5 mole) was carboxylated and the ionic nickel removed by Dowex 50-X8 ion-exchange resin. The reaction solution (302 ml.) gave the following analyses: total acidity, 0.57, 0.58 mole; ester, 0.34, 0.35 mole; olefin, 0.41, 0.41 mole; total hydrogen uptake (Pt), 0.60, 0.64 mole; acid formed by hydrogenolysis, 0.10, 0.12 mole.

Diazomethane (37.0 meq.) in ether was prepared from Aldrich Chemical Co. "Diazald" (N-methyl-N-nitroso-*p*-toluenesulfonamide, 21 g.) and was allowed to react with 19 ml. of carboxylation solution in the cold. The solution was distilled free of ether to yield 11.5 ml. of liquid residue. Vapor phase chromatographic analysis of the ester residue (3 m., Ucon polyalkylene glycol LB 1800X, 150°, 77 ml. He per min.) indicated a 2.4% yield of methyl methacrylate, a 34.4% yield of methyl α-(hydroxymethyl)acrylate, and a 42.2% yield of methyl α-(acetoxymethyl)acrylate.

Synthesis of α-(Acetoxymethyl)acrylic Acid.—Propargyl acetate was carboxylated with nickel carbonyl as described by Jones,[13] and a 30% yield of α-(acetoxymethyl)acrylic acid was obtained, m.p. 47–49° (hexane), lit.[13] m.p. 48–50°, 53°.

Synthesis of Ethyl α-(Hydroxymethyl)acrylate (IV) from α-(Acetoxymethyl)acrylic Acid.—α-(Acetoxymethyl)acrylic acid (48 g., 0.30 mole) was dissolved in absolute ethanol (500 ml.), and concentrated sulfuric acid (10 ml., 0.37 equiv.) was added as catalyst. The solution was refluxed for 16 hr., cooled, and the acid catalyst neutralized with 5 *N* sodium hydroxide. Ethanol was distilled water, was added (200 ml.), and the solution was extracted with three 200-ml. portions of chloroform. Distillation of the chloroform extracts yielded 32 g. (82%) of ethyl α-(hydroxymethyl)acrylate,[7] b.p. 70–71° (1 mm.), n^{22}D 1.4480.

Anal. Calcd. for $C_6H_{10}O_3$: sapon. equiv., 130; mol. wt., 130. Found: sapon. equiv., 129; mol. wt. (mercuric acetate titration for unsaturation), 129.

Carboxylation of Propargyl Alcohol with Nickel Carbonyl to Ethyl α-(Hydroxymethyl)acrylate (IV) and Ethyl *trans*-γ-Hydroxycrotonate (V).—Into a 1-l. round-bottom flask equipped with a stirrer, thermometer, Dry Ice cooled condenser, and dropping funnel were placed hydroquinone (5 g.), 95% ethanol (350 ml.), acetic acid (60 g., 1 mole), and nickel carbonyl (43 g., 0.25 mole). The solution was stirred and heated to 55°. Through a dropping funnel 1 ml. of the total propargyl alcohol (56 g., 1 mole) was added, and the mixture was allowed to stir until the color darkened and an exotherm was evidenced (2 min.). At this point the source of heat was removed, and the remainder of the propargyl alcohol was added dropwise at such a rate that the refluxing was under control. The addition took about 20 min., and the temperature reached 75–81° at the conclusion of the addition. The solution was allowed to stir for 15 min. and then concentrated sulfuric acid (14 ml., 0.25 mole) was added slowly with stirring. The flask then contained precipitated nickel sulfate hexahydrate and a yellow liquid phase, which gave a negative nickel test (dimethylglyoxime). The contents were filtered under reduced pressure (bromine trap for unchanged

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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.

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

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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

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