was washed with two 25-ml. portions of saturated calcium chloride solution and then with water to remove the methanol. After the mixture was dried for 16 hours over anhydrous magnesium sulfate and the drying agent removed, the low boiling fraction was flashed off under pressure of 15 mm. at 25° into a Dry Ice trap. At the Dry Ice temperature, about 1.5 g. of a solid, which was believed to be dimethyl carbonate, crystallized out. The crude triene was separated from this solid by a pipet, stabilized with 25 mg. of *t*-butylcatechol, and fractionated through a 6-inch, helix-packed column under nitrogen to yield 6.3 g. (18%) of impure 2-vinylbutadiene (I), b.p. 72° (752 mm.), n^{25}D 1.4634 [reported[8] b.p. 32° (200 mm.), n^{25}D 1.4559].

Anal. Calcd. for C_6H_8: C, 90.00; H, 10.00. Found: C, 90.20; H, 10.27.

The physical constants of this hydrocarbon plus the 58% yield of the Diels–Alder adduct X indicate that the 2-vinylbutadiene prepared in this manner is contaminated with isomeric hydrocarbons.

Fractionation of the higher boiling material from the pyrolysis through a 6-inch, helix-packed column produced 16.4 g. (32%) of methyl (2-methylenecyclobutyl)-methyl carbonate (IX), b.p. 56° (3 mm.), n^{25}D 1.4494, and 36.6 g. (37% recovery) of unreacted starting material VIII. IX readily decolorized bromine in carbon tetrachloride and could be pyrolyzed with the dicarbonate VIII to produce additional quantities of the triene I. No methyl allyl carbonate formed by cleavage of the cyclobutane ring was found.

$\Delta^{1(9)}$-Octalin-3,4,6,7-tetracarboxylic Anhydride (X).—To a solution of 2 g. (0.02 mole) of maleic anhydride and 25 mg. of *t*-butylcatechol in the smallest amount of toluene necessary for solution was added 0.5 g. of the crude 2-vinylbutadiene (I). Within 5 minutes a white flocculent precipitate formed and the solution became warm. After 1 hour the solid was removed by filtration and recrystallized three times from benzene–cyclohexane to yield 1.1 g. (58%) of $\Delta^{1(9)}$-octalin-3,4,6,7-tetracarboxylic anhydride (X), m.p. 240–242° (reported[8] m.p. 244–246°). Mixed melting point determination of X with an authentic sample[8] melted at 245–247°.

Simultaneous dehydrogenation and decarboxylation of the Diels–Alder adduct with 5% palladium-on-asbestos and copper chromite catalyst produced naphthalene, m.p. 78–79°. A mixed melting point with an authentic sample of naphthalene showed no depression.

All attempts to isolate an adduct resulting from the addition of 1 mole of 1,2-dimethylenecyclobutane and 1 mole of maleic anhydride were unsuccessful. Even in those experiments in which the diene was present in a molar excess, the product was always the adduct X.

In one case when 0.21 g. (0.0026 mole) of the triene I and 0.26 g. (0.0027 mole) of maleic anhydride were heated under reflux for 20 hours in benzene, a small amount, 134 mg. (26%), of a less-soluble adduct, m.p. 199–200°, was isolated. The adduct rapidly decolorized bromine in carbon tetrachloride. It is possible that the lower solubility of the diacid prevented the reaction from proceeding further.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.22; H, 6.12; mol. wt., 196. Found: C, 60.84; H, 6.15; mol. wt. (Rast), 209.

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM MONSANTO CHEMICAL COMPANY]

Studies on Polyvinyl Chloride. I. Reduction to a Hydrocarbon Polymer

BY JOHN D. COTMAN, JR.

RECEIVED OCTOBER 15, 1954

Polyvinyl chloride reacts with lithium aluminum hydride–lithium hydride in boiling tetrahydrofuran to yield a polyhydrocarbon. From the infrared spectrum of the product it was concluded that the product is quite similar to polyethylene. The reduction is complicated by atmospheric oxygen which is incorporated into the polymer as hydroxyl groups.

Marvel, Sample and Roy[1] have demonstrated the head-to-tail arrangement of monomer units in polyvinyl chloride by dechlorination with zinc.[2] The hydrocarbon product obtained is presumably a mixture of alicyclic structures. At high polymer dilution Freund dechlorination should yield a preponderance of cyclopropane structures. The removal of chlorines in pairs can result in complex three-dimensional structures at polymer concentrations favoring interchain reaction. In either case the molecular structures of the resulting hydrocarbons represent radical alterations of the polyvinyl chloride backbone.

Successful determination of branch ends in polyethylene by infrared analysis[3] and the possibility of chain branching in polyvinyl chloride revealed by the kinetic research of Bengough and Norrish[4] render highly desirable the conversion of polyvinyl chloride into a hydrocarbon of unchanged chain structure and molecular weight. Estimation of branches by infrared techniques on the polyhydrocarbon could be used as an index of branching in polyvinyl chloride if reduction did not involve chain cleavage, molecular rearrangement or extensive double bond formation.

It is uncertain whether procedures frequently employed for catalytic hydrogenation of chlorine compounds with chlorine removal, would result in molecular weight breakdown or rearrangement of polyvinyl chloride. Lack of accurate knowledge about adsorbed molecules on catalyst surfaces does not permit any judgement, *a priori*, on the probability of reduction without chain cleavage or rearrangement. Direct reduction with alkali metals or reduction through Grignard reagents do not offer clear routes to the desired polyhydrocarbon.

Eliel[5] has recently reported the preparation of optically active mono-α-deuteroethylbenzene by reaction between lithium aluminum deuteride and optically active phenyl methyl carbinyl chloride. The isolation of active hydrocarbon indicated nucleophilic displacement of chloride by the alumino deuteride as a preponderant, if not exclusive, reaction mechanism. The observations of Trevoy and Brown[6] suggest an SN2 mechanism in the reduction

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[1] C. S. Marvel, J. H. Sample and M. F. Roy, THIS JOURNAL, **61**, 3241 (1939); T. Alfrey, H. C. Haas and C. W. Lewis, *ibid.*, **73**, 2851 (1951).

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

[3] L. H. Cross, R. G. Richards and H. A. Willis, *Discs. Faraday Soc.*, **9**, 235 (1950); F. M. Rugg, J. J. Smith and L. H. Wartman, *J. Polymer Sci.*, **11**, 1 (1953); W. M. D. Bryant, and R. C. Voter, THIS JOURNAL, **75**, 6113 (1953).

[4] W. I. Bengough and R. G. W. Norrish, *Proc. Roy. Soc.* (*London*), **200**, 301 (1950).

[5] E. L. Eliel, THIS JOURNAL, **71**, 3970 (1949).

[6] L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

of primary and secondary aliphatic halides by lithium aluminum hydride.

Removal of halogen from polyvinyl chloride by nucleophilic hydride displacement should lead to a polyethylene of unchanged chain structure. Side reactions in the reduction of aliphatic chlorides by lithium aluminum hydride yield olefins particularly in the cases of tertiary halides and halogen alpha to an aromatic ring.[7] Olefin yields from primary and secondary halides are usually very low. There is no reported evidence of other side reactions for simple aliphatic halides. Such reduction should not result in chain scission, cross-linking or molecular rearrangement of polyvinyl chloride.

The conversion of polyvinyl chloride to a hydrocarbon polymer has been effected with both lithium aluminum hydride–lithium hydride in tetrahydrofuran and lithium aluminum hydride in tetrahydrofuran. Tetrahydrofuran is a solvent peculiarly suited for this polymer reduction because of its boiling point and also because it is one of the better mutual solvents for both polyvinyl chloride and lithium aluminum hydride. There are two distinct reaction periods in the reduction; a moderately rapid reaction to approximately 50% conversion, followed by extremely slow reduction of a colloidal phase of partially reduced polymer incompletely soluble in tetrahydrofuran. For concentrations of 0.16–0.20 M polyvinyl chloride (molarity based on monomer molecular weight) and 0.20–0.70 M total reducing agent reduction was 35–50% completed after 6 to 14 hours. One hundred forty hours were required for 92% reaction. To assure reduction complete to 95% or better, reaction under reflux was carried out for periods between 250 and 316 hours. Extent of reaction was determined by chlorine analysis of the reduced polymer or by measurement of liberated chloride ion. Concordant results were obtained by both analytical methods.

The polymeric hydrocarbon product was soluble in hot xylene and hot toluene. Cooling resulted in polymer separation. Infrared spectra of the polyhydrocarbons were similar to those of polyethylene and revealed a high degree of crystallinity,[8] *cf.* Fig. 1. Crystallization was thermally reversible, as for polyethylene, and not due to specimen orientation. Measurements of osmotic pressure in xylene at 89° indicated that reduction was not accompanied by appreciable molecular weight breakdown.

For the production of a polyhydrocarbon, it was found feasible to run the reaction in the absence of oxygen. The presence of air in the reaction vessel resulted in a low concentration of hydroxyl groups in the product. Polyhydrocarbon prepared under nitrogen is essentially free of hydroxyl. One reduction product obtained by interrupted reflux with intermittent exposure to air yielded a product with approximately one hydroxyl group/25 carbon atoms. These hydroxyl groups were confirmed by partial conversion to benzoate ester groups. The exact mechanism by which hydroxyl introduction occurs is obscure.

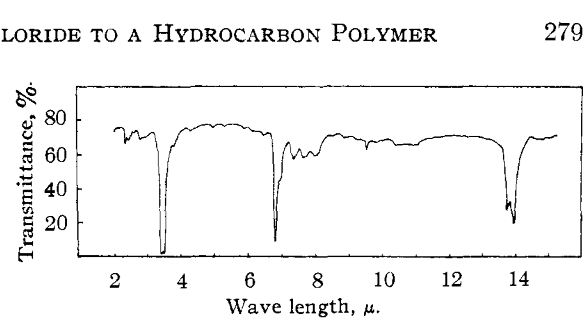

Fig. 1.—Infrared spectrum of a film of reduced polyvinyl chloride.

Experimental

Reduction of Polyvinyl Chloride.—Tetrahydrofuran was dried by distillation from potassium hydroxide followed by reflux over lithium aluminum hydride for five hours. The anhydrous solvent (b.p. 65–67°) was distilled directly into the reaction vessel or stored over calcium hydride under nitrogen.

A.—Five grams of polyvinyl chloride was dissolved in 300 cc. of anhydrous tetrahydrofuran under reflux. After solution of the polymer the vessel was swept with oxygen-free, dry nitrogen, then 0.5 g. of lithium aluminum hydride and 2.0 g. of finely powdered lithium hydride introduced. The reaction mixture was heated under reflux, with stirring, for 14 hours.

After cooling, distilled water was cautiously added to remove unreacted reducing agents. When hydrogen evolution had ceased, sufficient 1:1 nitric acid was added with warming to dissolve the basic aluminum salts. The precipitated polymer was washed free of inorganic salts by decantation and filtered. Washing on the filter was continued until the wash liquid gave no test for chloride ion. The polymer was dried for 48 hours under vacuum at 50°.

Sufficient silver nitrate solution was added to the washings to precipitate all chloride ion as silver chloride. The precipitate was digested and allowed to stand overnight. It was then filtered into a tared sintered glass funnel, washed well with diluted nitric acid and then distilled water. The dried precipitate corresponded to 34.3% reduction of polyvinyl chloride.

B.—Five grams of polyvinyl chloride, 1.5 g. of lithium hydride and 2.5 g. of lithium aluminum hydride in 400 cc. of anhydrous tetrahydrofuran reacted under reflux for 50 hours. Polymer isolation was as described in A. The liberated halide ion corresponded to 74.7% reduction.

Analysis for chlorine in the product was carried out by the Parr bomb method.[9] The percentage of reduction was determined from chlorine analysis of the product by use of the stoichiometric relationship

$$(\%\text{ of reduction}) = \frac{3550 - 6250\ (\%\text{Cl}/100)}{35.5 - 34.5\ (\%\text{Cl}/100)}$$

Halogen analysis indicated 77.5 ± 0.64% reduction. Conditions of reaction and results of additional runs are included in Table I.

TABLE I

REDUCTION OF POLYVINYL CHLORIDE

No.	Polyvinyl chloride[a] (g.)	$LiAlH_4$ (g.).[a]	LiH (g.)[a]	Time of reaction (hr.)	Reduction, %
1[c]	16.7	1.7	6.7	14	34.3
2	12.5	3.8	6.3	50	76.6
3	12.5[b]	12.5	2.5	143	91.5
4	10.0	6.0	0.0	8	41.6
5[c]	13.3[b]	13.3	0.0	316	97.0

[a] G./1000 cc. of tetrahydrofuran. [b] Soluble in hot xylene (90°) and hot toluene (90°); insoluble in either solvent at room temperature. [c] Flushed with nitrogen before reaction.

C. **Reduction of Polyvinyl Chloride in the Presence of Oxygen.**—Polyvinyl chloride and lithium aluminum hydride in amounts indicated in Table I, No. 5 reacted in tetrahydrofuran. Before heating the solution was flushed with

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(7) J. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948).

(8) R. S. Stein and G. B. B. M. Sutherland, unpublished observations.

(9) Direction Booklet No. 116 Parr Instrument Co., Moline, Ill., p. B11.

air. After 24 hours of reaction, reflux was discontinued and air admitted to the reaction vessel. Aeration was repeated after an additional 72 hours of reflux. Reaction was completed by refluxing for 224 hours. The product was isolated and free chloride ion determined. The result corresponded to 99% reaction. Chlorine analysis on the product indicated 97% reduction.

Infrared Spectra of Reduced Polyvinyl Chlorides.—The spectra of thin films of reduced polyvinyl chlorides, polyethylene and polyvinyl chloride were recorded on a Perkin-Elmer Model 21 double beam infrared spectrophotometer. A representative spectrum of a reduced polyvinyl chloride is reproduced in Fig. 1. A specially designed heated cell[10] was used to permit measurements at elevated temperatures.

Osomotic Molecular Weight Studies.—Mr. C. E. Woodard of these laboratories carried out the measurements of osmotic pressure, utilizing Zimm-Myerson[11] osmometers with cellophane membranes. Measurements on polyvinyl chloride were carried out at 30° in cyclohexanone. Reduced polyvinyl chloride was studied at 89° in xylene. Concentrations between 0.1 and 1.0% were employed and equilibrium π/C values extrapolated to zero concentration.

The number average molecular weight of polyvinyl chloride used in these studies was 89,000 ± 4,000, corresponding to a degree of polymerization of 1425. Complete reduction, without degradation should yield a polyhydrocarbon of number average molecular weight 39,900. Extrapolated π/C *vs.* C values for 91.5% reduced polyvinyl chloride (Table I, No. 3) gave a value $(\pi/C)_{c=0}$ of 0.43 in xylene at 89°. The number average molecular weight 68,000 ± 15,000 was higher than the 44,000 calculated for 91.5% reduction.

Esterification of Hydroxyl-containing Reduced Polyvinyl Chlorides.—A 1.0-g. portion of the product obtained by reduction in the presence of air (C) suspended in 10 cc. of pyridine was heated with 2 cc. of benzoyl chloride at 100° for 30 minutes. Excess benzoyl chloride was removed by soaking in aqueous 5% sodium bicarbonate. The product was soaked in water until free of pyridine and then in dilute ammonia. After thorough washing with distilled water the polymer was dried *in vacuo*.

Discussion

Comparison of the infrared spectra of polyethylene (DYNH), polyvinyl chloride and that of a reduced polyvinyl chloride (Table I, No. 5) which is presented in Fig. 1 leaves little doubt that the reduction of polyvinyl chloride by lithium aluminum hydride has produced a polyhydrocarbon quite like polyethylene. Characteristic absorption bands of polyethylene at 3.5, 6.85, 7.30 μ, and the doublet at 13.70 and 13.90 μ are all found in the reduced polymer spectrum at approximately the same relative intensities as in polyethylene. Intense absorption bands in the spectrum of polyvinyl chloride at 7.5, 9.2, 10.5, 12.1 and 14.5 μ are absent in the reduced polymer; absorption, at greatly reduced intensities at 7.0 and 8.0 μ are the last vestiges of intense polyvinyl chloride bands, and corroborate the results of chemical analysis that removal of chlorine has not been quantitative (97%). The well defined doublet at 13.70–13.90 μ has been interpreted by Stein and Sutherland[8] as due to the existence of hydrocarbon crystallites. On heating polyethylene and polyvinyl chloride reduced to 95% or better to temperatures around 135° the sharp doublet is replaced by a broadened single band of approximately equivalent integrated intensity with a single maximum at 13.90–13.95 μ. Cooling to room temperature is accompanied by reappearance of the doublet. The existence of crystallites which melt reversibly is characteristic of polyethylene.

From these observations it is concluded that reduction has, as a primary consequence, converted chloromethylene units into methylene groups. The spectra of several polymers reduced without nitrogen flushing have exhibited absorption of low intensity at 2.94 μ, presumably due to hydroxyl groups. To confirm the suspicion that atmospheric oxygen, rather than chance contaminant in the solvent was the source of hydroxyl in the reduced product, the reduction procedure C described in the Experimental section was devised. The infrared spectrum of this product reveals intense hydroxyl absorption at 2.94 μ as well as poorly defined absorption from 7.4–8.0 μ and 8.8–10.4 μ indicating the existence of –C–O– units. Comparison of the hydroxyl intensity with that of 3,9-diethyltridecanol-6 is the basis of an estimate of 1 hydroxyl/25 methylene groups in this product. The product is a largely amorphous polymer rather than a solid of definite melting point and cannot, as a consequence, have a preponderance of primary hydroxyl groups. The hydroxyl groups are probably distributed at random along the polymer backbone.

Conversion of these hydroxyl groups to benzoate ester units was only partially complete because of the insolubility of the polymer in pyridine. The spectrum of the partially esterified polymer has a band at 5.80 μ indicative of ester carbonyl. A concurrent reduction of hydroxyl concentration in the partially esterified polymer was concluded from observations on relative band intensities. Absorption at 6.86 μ has been assigned to a CH deformation mode characteristic of methylene groups. Conversion of a portion of the polymer hydroxyl to ester units will result in a decrease in the OH/CH$_2$ ratio of the polymer and a decrease in the ratio of band intensities characteristic of these chemical units. Ratios of transmittances at 2.94 and 6.86 μ for the oxygen containing polymer and its benzoate ester are 0.533 and 0.359, respectively. Although there is no certainty that the incorporation of a few benzoate groups into the polymer does not change the relative intensity coefficients of the absorptions in question the ester functions are so few in number that an estimate of 30–40% esterification from the intensity ratios is probably not very far wrong.

The number average molecular weight data reported for the polyvinyl chloride and for the reduced polymer do not correspond very well. The value for the reduced polymer is 54% higher than anticipated. Such a result could arise from several causes and does not necessarily invalidate the conclusion that lithium aluminum hydride reduction of polyvinyl chloride is uncomplicated by side reactions which alter the polymer backbone.

Experimental difficulties in the osmotic pressure measurements on the polyhydrocarbon were difficult to circumvent, particularly changes in membrane characteristics over prolonged periods of time.

There is a definite possibility that very low molecular weight material in the polyvinyl chloride may have been lost during the process of reduction and product isolation. The loss of a small percentage of low molecular weight material would result in higher number average molecular weights.

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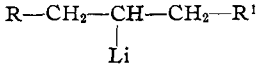
(10) G. C. Claver, unpublished observations.

(11) B. L. Zimm and I. Myerson, This Journal, **68**, 911 (1946).

Polymer association could be a contributing cause to the high number average molecular weights. The infrared spectrum revealed absorption of low intensity at 2.94 μ due to an estimated ratio of OH/CH_2 of 0.003–0.005.

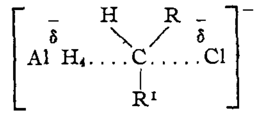
Trementozzi, *et al.*,[12] have demonstrated that the presence of relatively few hydroxyl groups in a hydrocarbon polymer can lead to polymer association in non-polar solvents. The hydroxyl groups in reduced polyvinyl chloride are probably causing association in xylene, even at 89°. It is questionable that the few remaining chlorines could be producing associated polyvinyl chloride like clusters. The observation that most of the hydroxyl groups must be along the polymer backbone has as a consequence that introduction of hydroxyl into the polymer does not necessarily correspond to chain scission.

There is no clear cut explanation of the route by which oxygen is introduced in the polymer during reduction. Direct oxidation of polymer to groups which are subsequently reduced cannot be excluded. However, the ready reaction of lithium aluminum hydride in solution[13] with oxygen to yield hydrogen gas, suggests that the oxygen concentration in solutions of lithium aluminum hydride is negligible. It is a reasonable assumption that alumino hydride ion is oxidized to an oxyanion of indefinite structure, liberating hydrogen. Displacement of chloride by such an oxyanion could lead to a product which on hydrolysis would yield a secondary hydroxyl group. This mechanism of hydroxyl introduction, speculative as it is, is not unreasonable. An alternative mechanism of hydroxyl introduction into the polyhydrocarbon has been considered. Oxidation of a secondary alkyl lithium produced by reaction between lithium aluminum hydride and secondary halide



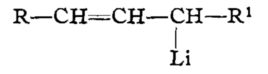
$$R{-}CH_2{-}\underset{\displaystyle Li}{\underset{|}{CH}}{-}CH_2{-}R^1$$

could be involved. This does not necessarily imply such an organolithium intermediate in the reduction process. The weight of evidence[5,6] on the mechanism of reaction between alkyl halides and lithium aluminum hydride favors nucleophilic displacement on carbon



$$\left[\overset{\delta -}{\text{Al H}_4}\cdots\cdot\underset{\displaystyle R^1}{\underset{|}{\overset{\text{H}\ \diagdown\ \diagup\ \text{R}}{\text{C}}}}\cdots\cdot\overset{\delta -}{\text{Cl}}\right]^-$$

halogen departing as halide ion as the negative aluminohydride complex approaches the carbon from the backside. The incidence of organolithium intermediates of the halides of acidic hydrocarbons such as diphenylmethane and fluorene during reduction with lithium aluminum hydride has been reported.[6] However, there has been no clear evidence of such organolithium intermediates as transient species in the reduction of simple alkyl monohalides. The detailed fine structure of polyvinyl chloride is still a matter for conjecture. Unsaturation in the polymer chain may favor the formation of α,β unsaturated organometallic compounds, *e.g.*



$$R{-}CH{=}CH{-}\underset{\displaystyle Li}{\underset{|}{CH}}{-}R^1$$

SPRINGFIELD, MASS.

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[12] Q. A. Trementozzi, R. F. Steiner and P. Doty, THIS JOURNAL, **72**, 2070 (1952); Q. A. Trementozzi, *J. Phys. Colloid Chem.*, **54**, 1227 (1950).

[13] W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., p. 472; Hochstein, THIS JOURNAL, **71**, 305 (1949).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

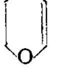
Reactions of 2,3-Dihydropyran[1]

BY CHARLES D. HURD, JAMES MOFFAT AND LUIGI ROSNATI

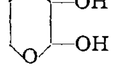
RECEIVED JANUARY 14, 1955

In the hydroxylation of 2,3-dihydropyran (I) to 3,4-dideoxypentose (II) some closely-related, unidentified material also is formed which gives rise to formaldehyde on periodate cleavage. It is possible to purify II by careful fractional distillation of the acetyl derivative. Hydroxylation of I by means of aqueous sodium chlorate and osmium tetroxide gives II, but in poor yield. N-Bromophthalimide adds to I, yielding a phthalimidobromotetrahydropyran. Several new hydrazones and osazones of II are reported.

In previous work[2,3] it was shown that 2,3-dihydropyran (I) could be hydroxylated to yield 3,4-dideoxypentose(II). The latter should give rise to 4-hydroxybutanal and formic acid on periodate oxidation, but in the present work we observed that a large amount of formaldehyde was obtained. This unexpected result led to the examination of the reactions involved with the purpose of finding a way of of getting pure 3,4-dideoxypentose and of discovering, if possible, the source of the formaldehyde produced in the periodate cleavage. The former objective has been satisfactorily achieved, the latter only in part.



I



II

The suspicion that the dihydropyran may have contained 2-methylenetetrahydrofuran (III) caused us to inspect critically the evidence used in proof of

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[1] This paper reports research undertaken in coöperation with the Quartermaster Food and Container Institute for the Armed Forces, and has been assigned number 526 in the series of papers approved for publication. The views or conclusions contained in this report are those of the authors. They are not be construed as necessarily reflecting the views or indorsement of the Department of Defense.

[2] C. D. Hurd and C. D. Kelso, THIS JOURNAL, **70**, 1484 (1948).

[3] C. D. Hurd and O. E. Edwards, *J. Org. Chem.*, **14**, 680 (1949).