androsten-3-one, XXVI). A suspension of 6-dehydro-9α-fluoro-11β-hydroxy-17α-methyltestosterone (100 mg.) in 1 ml. of thiolacetic acid was refluxed for 18 hr., solution being complete after approximately 25 min. The solution was evaporated to dryness. Trituration of the residual solid with ether afforded 88 mg. (72%) of XXVI, m.p. 241° dec. Several recrystallizations from acetone–petroleum ether gave white crystals, m.p. 243–246° dec.; $[\alpha]_D^{25}$ −41° (0.24% in chloroform); λ_{max} 236 mμ (ϵ 19,600); λ_{max} 2.91, 5.94, 6.04, 6.15, 8.0 μ.

Anal. Calcd. for $C_{22}H_{31}FO_4S$: C, 64.37; H, 7.61; F, 4.62; S, 7.81. Found: C, 63.68; H, 7.93; F, 4.42; S, 7.85.

17β-Acetoxy-7α-methylthioandrostan-3-one (XXIX). A solution containing 2.0 g. of 17β-acetoxy-7α-methylthio-4-androsten-3-one (XVI) in 25 ml. of dioxane and 25 ml. of ether was added dropwise to a solution of lithium (300 mg.) in 250 ml. of liquid ammonia over a period of 15 min. After stirring for an additional 35 min. the blue color of the solution was discharged by the addition of 6.0 g. of ammonium chloride and the ammonia was allowed to evaporate. The residue was distributed between ether and water, and the water extract was washed several times with methylene chloride. The combined organic extracts were washed with water, dried with anhydrous magnesium sulfate and evaporated to dryness leaving 1.6 g. of amorphous material. As at least partial deacetylation apparently had occurred (hydroxyl absorption at 2.89 μ), the material was acetylated with acetic anhydride in pyridine solution at room temperature overnight. After dilution with water, the mixture was extracted with methylene chloride, washed with water, dried over anhydrous magnesium sulfate, and evaporated to dryness leaving a syrup. Trituration with ether and filtration afforded 720 mg. (36%) of 17β-acetoxy-7α-methylthioandrostan-3-one (XXIX) as a white powder, m.p. 175–179°. The material had no ultraviolet absorption; $[\alpha]_D^{25}$ − 44.4° (0.61% in chloroform); λ_{max} 5.75, 5.80, 8.00 μ.

Anal. Calcd. for $C_{22}H_{34}O_3S$: C, 69.79; H, 9.05; S, 8.47. Found: C, 69.80; H, 9.15; S, 8.55.

17β-Hydroxy-2-hydroxymethylene-7α-methylthioandrostan-3-one (XXXI).[26] Sodium hydride (2.24 g. of a 50% dispersion in oil) was added to a solution of 2.8 g. of 17β-acetoxy-7α-methylthioandrostan-3-one (XXIX) in 100 ml. of reagent benzene (freed from moisture by azeotropic distillation of 20 ml.) containing 5.6 ml. of ethyl formate. The reaction mixture was allowed to stand under nitrogen for 5 days. Methanol (5.6 ml.) was then added to decompose the excess hydride, and the solution was diluted with 280 ml. of benzene and 280 ml. of water. The layers were separated and the aqueous phase was extracted with benzene. The aqueous layer was then acidified with dilute hydrochloric acid and the precipitated enol was extracted with ether. The extracts were washed with water, dried with anhydrous magnesium sulfate, and evaporated to dryness to give a glass. Crystallization from acetone–petroleum ether gave 1.6 g. (60%) of XXXI, m.p. 130–140° (gas). The compound gave a deep red color with 1% alcoholic ferric chloride solution. Recrystallization from ethyl acetate afforded white crystals, m.p. 163–165° (previous softening); $[\alpha]_D^{25}$ −29.2° (1.4% in chloroform); λ_{max} 282 mμ (ϵ 7,300); λ_{max} 2.88, 6.10, 6.25 μ.

Anal. Calcd. for $C_{21}H_{32}O_3S$: C, 69.20; H, 8.85; S, 8.80. Found: C, 69.54; H, 9.01; S, 8.43.

17β-Hydroxy-7α-methylthioandrostano[3,2-c]pyrazole (XXX). To a solution of 200 mg. of 17β-hydroxy-2-hydroxymethylene-7α-methylthioandrostan-3-one (XXXI) in 7 ml. of absolute alcohol was added 3.0 ml. of absolute alcohol containing 0.03 ml. of 98–100% hydrazine hydrate. The solution became turbid and a crystalline material separated after 10 min. The mixture remained colorless when tested with 1% alcoholic ferric chloride solution. The mixture was cooled and filtered to give 181 mg. of product (XXX) in two crops, m.p. 170–173° (gas). Several recrystallizations from acetone-water gave white crystals, m.p. 174° (gas); $[\alpha]_D^{25}$ −22.2° (0.4% in chloroform); λ_{max} 223 mμ (ϵ 4,750); λ_{max} 3.05, 6.90, 10.46 μ.

Anal. Calcd for $C_{21}H_{32}N_2OS \cdot {}^1/_2H_2O$: C, 68.24; H, 9.00; N, 7.58; S, 8.68. Found: C, 68.14; H, 9.09; N, 8.09; S, 8.64

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PEARL RIVER, N. Y.

[CONTRIBUTION FROM THE NATURAL PRODUCTS RESEARCH DEPARTMENT, SCHERING CORP.]

Enol Ethers of Steroidal Δ^4-3-Ketones

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A method is described for the preparation of a number of unsaturated steroidal enol ethers, involving alkoxyl interchange between Δ^4-3-ketones, 2,2-dimethoxypropane, and alcohols.

Recently, Tanabe and Bigley[1] described a new method to protect the hydroxyl groups of the dihydroxyacetone side chain typical of the cortical steroids. This procedure involves acid-catalyzed ketal interchange between 2,2-dimethoxypropane and the corticoid to be protected to produce 17α,21-isopropylidenedioxy steroids. In connection with another problem, we had occasion to apply this reaction to 17α,21-dihydroxy-Δ^4-pregnen-3,20-dione, Reichstein's S (I). When the reaction was allowed to proceed until a small aliquot was negative to the TPTZ color reagent (disappearance of the dihydroxyacetone side chain)—this occurred after two and one-half hours—the desired 17α,21-isopropylidenedioxy derivative II was isolated. However, a second product, considerably

(1) Masato Tanabe and Barbara Bigley, *J. Am. Chem. Soc.*, **83**, 756 (1961).

less polar in paper chromatograms, appeared to be a contaminant. In fact, when the reaction period was extended to five hours, only the second material was obtained. Elemental analysis of this less polar substance indicated a molecular formula of $C_{25}H_{36}O_4$, *i.e.*, II plus CH_2. The infrared spectrum lacked the characteristic Δ^4-3-ketone bands, but showed instead the typical doublet observed for $\Delta^{3,5}$-3-enol ethers.[2]

The negative optical rotation also pointed toward unsaturation at C-5 and C-6. Accordingly, the new product was formulated as 17α,21-isopropylidenedioxy-3-methoxy-$\Delta^{3,5}$-pregnadiene-3,-20-dione (III). There is precedence for this reaction: as far back as 1938, Serini and Köster[3] prepared the 3-ethyl enol ether of androstenedione by means of acetone diethyl ketal.[4]

Enol ethers of this type have recently become important intermediates in the synthesis of substituted steroid hormones. Thus, 6-fluoro[5] or 6α-methyl[6] derivatives were prepared by the reaction of enol ethers with perchloryl fluoride and polyhalomethanes, respectively. Furthermore, a recent communication[7] concerning paradoxical dependency of the biological activity of Δ^4-3-keto steroidal enol ethers on the route of administration makes their preparation of interest in their own right.

Such steroidal enol ethers have conventionally been obtained by acid-catalyzed treatment with orthoformic esters.[3,8] Ercoli and Gardi[7] summarized alternate approaches, such as direct reaction of a Δ^4-3-one with an alcohol by azeotropic codistillation or acid-catalyzed enol ether interchange. Since interchange reactions with low molecular weight ketals appeared to be very mild and convenient, we decided to examine the scope of the above reaction.

As a convenient and simple model compound we used testosterone acetate (IVa). This material was indeed converted to the expected methyl enol ether Va by reflux for three and one-half hours in a 2,2-dimethoxypropane–dimethylformamide solution containing *p*-toluenesulfonic acid. Omission of the ketal did not effect the desired conversion. Structure follows from analysis, physical properties, and subsequent reconversion to testosterone (Va[1]) under conditions designed to cleave enol ethers.[9]

It would appear, then, that dimethoxypropane would be useful in the generation of enol ethers of steroidal Δ^4-3-ketones. We confirmed the observation of Serini and Köster[3] that the method is specific for the latter moiety; thus, Δ^4-androsten-3,17-dione (IVb) gave 3-methoxy-$\Delta^{3,5}$-androstadien-17-one (Vb). Again, in the pregnane series, ring A only is involved; progesterone (IVc) gave 3-methoxy-$\Delta^{3,5}$-pregnadien-20-one (Vc). A more demanding case was $\Delta^{4,16}$-pregnadiene-3,20-dione, since one might have expected here a lesser degree of discrimination between two α,β-unsaturated ketones. The single product (VII) isolated, however, again clearly indicated preferential reaction at the ring A enone site.[10]

A detailed study has recently been published on the preparation of *ketals* by acid catalyzed interchange of ketones with 2,2-dimethoxypropane.[13] These authors observed that under acid conditions the ketals would sometimes lose a molecule of alcohol to form enol ethers. Since this was an undesirable side reaction in their work, and since it was appreciable already at fairly low temperatures (50°),[14] they went to special pains to suppress it by neutralizing with alkali prior to workup.

It does not seem likely, however, that the enol ethers here described are formed *via* the ketals; we believe that the intermediate unsaturated hemiketal loses water directly (see Fig. 1). The conditions employed are just vigorous enough to produce these unsaturated steroidal A ring enol ethers without at the same time resulting in ketal interchange (or further enol ether formation) elsewhere in the molecule.

Lorette and Howard[13] were able to prepare ketals of various alcohols by coupling the direct combination of the ketone and alcohol in question with the hydrolysis of 2,2-dimethoxypropane. This same method may also be applied to the formation of unsaturated enol ethers. 20β-Acetoxy-Δ^4-pregnen-3-one (IVd) was allowed to interact

(2) H. Rosenkranz and M. Gut, *J. Org. Chem.*, **25**, 445 (1960).

(3) A. Serini and H. Köster, *Ber.*, **71**, 1766 (1938).

(4) We are grateful to Dr. Ercoli for pointing out to us this little-known fact.

(5) S. Nakanishi, K. Morita, and E. V. Jensen, *J. Am. Chem. Soc.*, **81**, 5259 (1959).

(6) S. Liisberg, W. D., Godtfredsen, and S. Vangedal, *Tetrahedron*, **9**, 149 (1960).

(7) A. Ercoli and R. Gardi, *J. Am. Chem. Soc.*, **82**, 746 (1960). See also A. Ercoli, G. Bruni, G. Falconi, R. Gardi, and A. Meli, *Endocrinol.*, **67**, 521 (1960).

(8) See also E. Schwenk, G. Fleischer, and B. Whitman, *J. Am. Chem. Soc.*, **60**, 1702 (1938).

(9) Acid hydrolysis produced a mixture of testosterone acetate and the free alcohol. This was subjected to a base treatment to assume complete ester removal.

(10) This specificity in enol ether formation is also encountered by the conventional ortho ester method.[3] The German authors themselves observed it for androstenedione. Sandoval, *et al.*[11] encountered the same situation in the corresponding 19-nor- compound. Uskoković *et al.* observed ring A specificity for 17α-hydroxyprogesterone.[12] The entire subject has been reviewed by H. J. E. Loewenthal, *Tetrahedron*, **6**, 269 (1960).

(11) A. Sandoval, L. Miramontes, G. Rosenkranz, C. Djerassi, and F. Sondheimer, *J. Am. Chem. Soc.*, **75**, 4117 (1953).

(12) M. Uskoković, M. Gut, and R. I. Dorfman, *J. Am. Chem. Soc.*, **81**, 4561 (1959).

(13) N. M. Lorette and W. L. Howard, *J. Org. Chem.*, **25**, 521 (1960); W. L. Howard and N. B. Lorette, *J. Org. Chem.*, **25**, 525 (1960).

(14) In the steroid series, saturated ketals have been converted to enol ethers: See E. P. Oliveto, C. Gerold, and E. B. Hershberg, *J. Am. Chem. Soc.*, **76**, 6113 (1954).

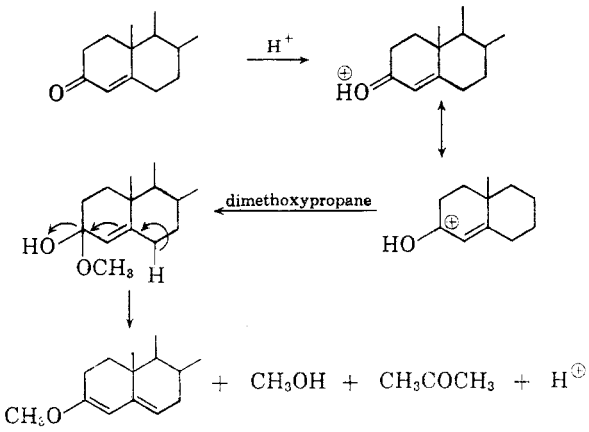
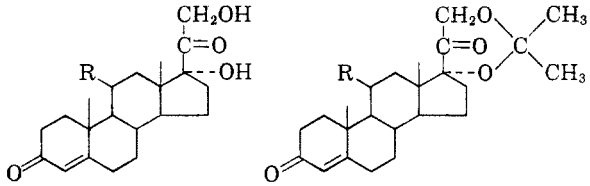


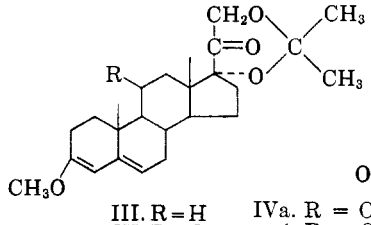
Figure 1

with ethanol under the usual conditions in dimethylformamide/2,2-dimethoxypropane. The resulting product turned out to be the ethyl enol ether Vd, identical with a reaction product synthesized by the classical ethyl orthoformate procedure of Serini and Köster.[3] A similar coupling reaction with the latter procedure, to produce enol ethers of a variety of alcohols, has also been described by Ercoli and Gardi.[7]

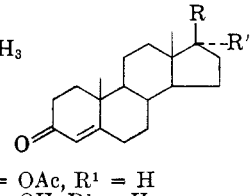


I. R = H
VIII. R = OH

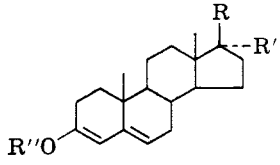
II. R = H



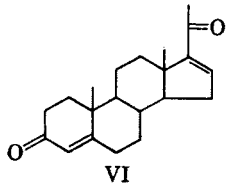
III. R = H
IX. R = OH



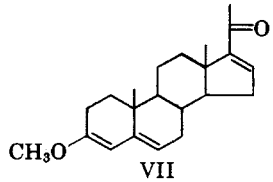
IVa. R = OAc, R^1 = H
a[1]. R = OH, R^1 = H
b. R,R^1 = O
c. R = —$COCH_3$, R^1 = H
d. R = —C(OAc)CH_3, R^1 = H



Va. R = OAc, R^1 = H, R^{11} = CH_3
b. R,R^1 = O, R^{11} = CH_3
c. R = —$COCH_3$, R^1 = H, R^{11} = CH_3
d. R = —C(OAc)CH_3, R^1 = H, R^{11} = C_2H_5



VI



VII

Finally, the reaction originally observed with Compound S (I) was carried out with hydrocortisone (VIII). As expected, the isopropylidenedioxy enol ether IX was obtained in good yield. The method is thus seen to be applicable in a wide variety of structures. Ring A dienones, however, do not form enol ethers under these conditions.[1]

EXPERIMENTAL[14]

17α,21-Dihydroxy-Δ^4-pregnene-3,20-dione 17,21-acetonide (II). Reichstein's Compound S (I) (10 g.) was dissolved in 150 ml. of 2,2-dimethoxypropane and 50 ml. of dimethylformamide. *p*-Toluenesulfonic acid (260 mg.) was added, and the solution was refluxed for 2.5 hr., when a positive TPTZ test had vanished. The solution was cooled and neutralized with 1.5 g. of solid sodium bicarbonate, filtered and concentrated *in vacuo*. The residual oil was chromatographed over 300 g. of neutral alumina. From the benzene eluates, 6.9 g. of material was obtained, m.p. 176–203°, paper-chromatographically homogeneous. An analytical sample was obtained by recrystallization from acetone-isopropyl ether; m.p. 196–202, λ^{Nujol} at 5.80, 6.00, and 6.18 μ; ϵ_{240} 16,800; $[\alpha]_D^{22}$ + 107.4.

Anal. Calcd. for $C_{24}H_{34}O_4$: C, 74.57; H, 8.87. Found: C, 74.86; H, 9.00.

3,17α,21-Trihydroxy-$\Delta^{3,5}$-pregnadien-20-one 17,21-acetonide 3-methyl ether (III), R = H). Reichstein's Compound S (I) (300 mg.) was allowed to react under the conditions described in the preceding section, the only difference being an extension of the reaction period to 4.75 hr. Work-up gave a filterable solid, 133 mg., m.p. 130–156°. An analytical sample obtained from acetone-methanol containing a drop of pyridine had a m.p. of 141–161°,[15] ϵ_{237} 21,300 λ^{Nujol} at 5.82, 6.05, and 6.14 μ; $[\alpha]_D^{24}$ − 96.7.

Anal. Calcd. for $C_{25}H_{36}O_4$: C, 74.96; H, 9.06. Found: C, 74.69; H, 8.89.

3-Methoxy-$\Delta^{3,5}$-androstadien-17β-ol acetate (Va). 17β-Acetoxy-Δ^4-androsten-3-one (IVa) (1 g.) was dissolved in 5 ml. of dimethylformamide and 5 ml. of 2,2-dimethoxypropane. *p*-Toluenesulfonic acid monohydrate (26 mg.) and 0.2 ml. of methanol were added, and the resulting solution was refluxed for 3.5 hr. Excess acid was neutralized with 150 mg. of sodium bicarbonate and the reaction mixture was partitioned between water and ethyl ether. The organic layer was dried and concentrated. Crystallization from acetone gave a first crop of 486 mg. of 3-methoxy-$\Delta^{3,5}$-androstadien-17β-ol acetate. An analytical sample was obtained by recrystallization from acetone and possessed m.p. 154–172°; λ^{Nujol} 5.77 (acetate), 6.03, 6.17 (enol ether doublet), 8.65 (C—O stretching of acetate) and 9.70 μ (enol ether); ϵ_{239} 20,000; $[\alpha]_D^{24}$ − 47.

Anal. Calcd. for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 77.03; H, 9.50.

Reconversion to testosterone. The foregoing enol ether (100 mg.) was dissolved in 2.2 ml. of methanol, 0.11 ml. of 2*N* hydrochloric acid was added, and the solution was allowed to stir overnight at room temperature. The steroid was then precipitated with 40 ml. of ice water and filtered to give 83 mg. of a mixture of testosterone acetate and free alcohol (infrared). Accordingly, homogeneity was assured by alkaline hydrolysis. The material was dissolved in 10 ml. of 5%

(14) All melting points were taken on a Kofler block and are uncorrected. Rotations were taken in a 1-dm. tube at a concentration of *ca.* 1% in chloroform. Ultraviolet spectra were taken in methanol. Analyses and spectrographic data were obtained by the Microanalytical and Physical Chemistry Departments of these Laboratories.

(15) The enol ethers have wide melting ranges. Their homogeneity was determined by paper mobility in several systems.

methanolic potassium hydroxide and refluxed for 2 hr., the solution was cooled and neutralized with glacial acetic acid, precipitated in excess ice water, and extracted into ether. The organic layer was washed, dried, and concentrated to give, upon crystallization from isopropyl ether, 45 mg. of testosterone, identical with genuine material by melting point, mixed melting point, and infrared spectrum.

3-Methoxy-$\Delta^{3,5}$-androstadien-17-one (Vb). Δ^4-Androstene-3,17-dione (IVb.) (1.0 g.) was dissolved in 5 ml. of 2,2-dimethoxypropane, and 5 ml. of dimethylformamide *p*-toluenesulfonic acid monohydrate (26 mg.) and 0.2 ml. of methanol were added (resultant *p*H = 6) and the solution was refluxed for 3.5 hr. After cooling, it was neutralized with 152 mg. of sodium bicarbonate and added dropwise to a rapidly stirring mixture of ice water. After 20 min., the resulting oil had solidified and was filtered to give 1.1 g. of product. Paper chromatographic investigation showed it to be mainly enol ether (in the heptane–Methyl Cellosolve system, $R_f = 0.61$) with some starting material ($R_f = 0.16$) and an unidentified non-polar contaminant ($R_f = 0.91$) also present. Recrystallization from acetone-methanol (containing a drop of pyridine) gave 494 mg. of paper-chromatographically homogeneous enol ether, m.p. 141–163°; λ^{Nujol} at 5.78 (17-ketone), 6.06 and 6.15 μ. (enol ether); ϵ_{239} 20,000; $[\alpha]_D^{24} - 84.4$.

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 79.95; H, 9.39. Found: C, 80.28; H, 9.24.

3-Methoxy-$\Delta^{3,5}$-pregnadien 20-one (Vc). Progesterone (IVc) (300 mg.) was dissolved in 2.5 ml. of 2,2-dimethoxypropane and an equal volume of dimethylformamide *p*-toluenesulfonic acid monohydrate (8 mg.) and 0.1 ml. of methanol were added, and the solution refluxed for 3.5 hr. After cooling and neutralization with 45 mg. of sodium bicarbonate, the solution was slowly added to 200 ml. of ice water, stirred for 0.5 hr. and filtered. The enol ether thus obtained (288 mg.) had λ^{Nujol} at 5.90 (C-20-ketone) 6.06 and 6.15 μ (enol ether doublet). Recrystallization from acetone-methanol containing a trace of pyridine gave an analytical sample, m.p. 135–160°; $[\alpha]_D^{23} - 61.4°$; ϵ_{239} 20,000; infrared spectrum identical with the crude product.

Anal. Calcd. for $C_{22}H_{32}O_2$: C, 80.44, H, 9.83. Found: C, 80.76; H, 9.85.

3-Methoxy-$\Delta^{3,5,16}$-pregnatrien-20-one (VII). $\Delta^{4,16}$-Pregnadiene-3,20-dione (VI) (300 mg.) was subjected to enol-etherification conditions as above. A crude yield of 316 mg. was obtained. An analytical sample from acetone-methanol (trace of pyridine) had a m.p. of 152–167°; λ^{Nujol} at 5.99 (20-one), 6.04, 6.13 (enol ether), and 6.30 (Δ^{16}) μ ϵ_{239} 28,000; $[\alpha]_D^{23} - 109.4°$.

Anal. Calcd. for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26. Found: C, 81.05; H, 9.20.

3-Ethoxy-$\Delta^{3,5}$-pregnadien-20β-ol acetate (Vd). 20β-Acetoxy-Δ^4-pregnen-3-one (IVd) (1 g.) was dissolved in 5 ml. of dimethylformamide and an equal volume of 2,2-dimethoxypropane. Ethanol (10 ml.) and 26 mg. of *p*-toluenesulfonic acid monohydrate were added, and the solution refluxed for 4 hr. It was then cooled and poured into an excess of ice water. The oily suspension was extracted with ether, dried, and concentrated. After overnight standing in the refrigerator and trituration with isopropyl ether, the enol ether crystallized and was filtered off. The product had λ^{Nujol} 5.79 (acetate), 6.02 and 6.11 (enol ether), 8.02 (acetate C—O), and 8.54 μ (ether C—O). It was identical with a product prepared *via* the classical ethyl orthoformate method of Serini and Köster: m.p. 102–117°, $[\alpha]_D^{24} - 94.8$, ϵ_{240} 18,900.

Anal. Calcd. for $C_{25}H_{38}O_3$: C, 77.67; H, 9.91. Found: C, 77.68; H, 9.79.

3,11β,17α,21-Tetrahydroxy-$\Delta^{3,5}$-pregnadien-20-one 17,21-acetonide 3-methyl ether (IX). Hydrocortisone (VIII) (15 g.) was dissolved in 225 ml. of 2,2-dimethoxypropane and 75 ml. of dimethylformamide. *p*-Toluenesulfonic acid monohydrate was added, and the resulting solution was refluxed for 3 hr. After cooling, 2.3 g. of sodium bicarbonate was added, and the suspension shaken and filtered. Vacuum concentration of the filtrate gave an oil that crystallized after overnight standing with methanol. Filtration gave 8.2 g. of the acetonide enol ether, m.p. 147–195° (homogeneous by paper chromatography). Recrystallization from acetone-methanol gave an analytical sample, m.p. 152–183°; λ^{Nujol} at 2.81 (OH), 5.86 (C-20-ketone), 6.02 and 6.14 μ (enol ether), ϵ_{238} 19,800.

Anal. Calcd. for $C_{25}H_{36}O_5$: C, 72.08; H, 8.71. Found: C, 71.87; H, 8.71.

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[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Acid Epimerization of D-Glucose[1a]

YASUO OHNO[1b] AND KYLE WARD, JR.

Received October 13, 1960

The formation of small amounts of fructose from glucose by heating with dilute sulfuric acid under the conditions of cellulose hydrolysis has been corroborated, but not that of mannose. The fructose was isolated by paper chromatography and definitely identified by means of infrared spectrography. Ost's early experiments on the acid epimerization of glucose were similarly corroborated. The possibility of such conversions must be considered in interpreting the analyses of plant carbohydrates.

Shortly after paper chromatography began to prove useful in the analysis of plant polysaccharides, it was pointed out[2] that great care had to be taken during neutralization of the hydrolyzates as isomerization of glucose to fructose could occur at a *p*H greater than 4.0. Since the epimer mannose can also be formed,[3] this becomes a matter of some importance in the analysis of the sugars in the hydrolyzates from plant materials.[4,5]

(1)(a) Presented at the 138th National Meeting of the American Chemical Society, New York, N.Y., Sept. 11–16, 1960. (b) Research Fellow from Tokyo University of Agriculture and Technology, Tokyo, Japan.

(2) J. Sundman, *Paperi ja Puu*, **32**, 306 (1950).

(3) J. C. Speck, Jr., *Advances in Carbohydrate Chemistry*, Vol. 13, Academic Press, New York, 1958, pp. 63–103.

(4) A. Roudier and L. Eberhard, *Mem. serv. chim. etat*, **37**, 231 (1952).

(5) A. Roudier and L. Eberhard, *Comptes rendus*, **235**, 207 (1952).