(B) Rearrangement of (III) to (V).—Nine and eight-tenths grams of III was treated with 14.1 g. of freshly distilled methyl iodide. The mixture was then heated in a sealed tube at 50–60° for eight hours. After the tube was opened, the excess of methyl iodide was removed by a blast of air and the residue distilled under a vacuum. Compound V when pure boils at 180–182° under 4.5 mm. pressure and solidifies on slow cooling. The yield was quantitative. For analysis, it was recrystallized from petroleum ether, separating in needles.

Anal. Calcd. for $C_{10}H_{16}O_2N_2$: N, 14.28. Found: N, 14.16.

The structure of the compound was established by its behavior on hydrolysis, giving X.

Formation of X.—Compound V was heated with dilute hydrochloric acid for one hour. The solution was evaporated to dryness on a water-bath and the residue dissolved in hot water, whereupon X crystallized on cooling in colorless needles, melting at 148–150°.

Anal. Calcd. for $C_9H_{14}O_2N_2$: N, 15.38. Found: N, 15.50, 15.47.

(C) Rearrangement of the Partially Rearranged Pyrimidine (V) into the Completely Rearranged Pyrimidine (IV).—Five grams of V was heated at 330–350° for six to eight hours. The reaction mixture solidified on cooling. It dissolved in a little hot benzene, to which petroleum ether was added just to turbidity, whereupon (IV) separated in needles, melting at 74–75°. It proved to be identical with 1,3,4-trimethyl-5-*n*-propyluracil (IV) obtained by heating pyrimidine (III).

Anal. Calcd. for $C_{10}H_{16}O_2N_2$: N, 14.28. Found: N, 14.41, 14.55.

Summary

1. The action of phosphorus oxychloride on 4-methyl-5-*n*-propyluracil produces 4-methyl-5-*n*-propyl-2,6-dichloropyrimidine.

2. This 2,6-dichloropyrimidine reacts with sodium methylate and with sodium ethylate in a characteristic manner, giving the corresponding 2,6-dimethoxy-pyrimidine, and 2,6-diethoxy-pyrimidine derivatives, respectively.

3. 4 - Methyl - 5 - *n* - propyl - 2,6 - dimethoxy-pyrimidine and 2-oxy-3,4-dimethyl-5-*n*-propyl-6-methoxy-pyrimidine can be rearranged to their isomeric and stable *lactam* modification, 1,3,4-trimethyl-5-*n*-propyluracil, on heating at an elevated temperature. On the other hand, 4-methyl-5-*n*-propyl-2,6-dimethoxy-pyrimidine rearranges only partially on heating with methyl iodide at 50–60° to 2-oxy-3,4-dimethyl-5-*n*-propyl-6-methoxy-pyrimidine.

Oxidation of Glycosides by Means of Lead Tetraacetate in Aqueous Solution

BY J. M. GROSHEINTZ

In a previous paper[1] there was described a new technique for the application of lead tetraacetate as an oxidizing agent. It was shown that the cleavage of the carbon chain in compounds containing two and three adjacent hydroxyl groups could be carried out in aqueous solution as well as in non-aqueous solution. Lead tetraacetate therefore can replace periodic acid in most instances in which aqueous solvents are required.

E. L. Jackson and C. S. Hudson,[2] in their determination of ring structure and alpha- and beta-configuration of glycosides, thoroughly investigated the cleavage of the carbon chain of a number of glycosides by oxidation with periodic acid. In the present paper parallel experiments with lead tetraacetate are reported in order to show the similar action of this reagent on glycosides in aqueous solution.[3] Starting with the optical antipodes of two glycosides used by E. L. Jackson and C. S. Hudson[2] the oxidation products and their derivatives were compared with the products already known.

The oxidation of alpha- (I) and beta-methyl-*l*-arabinopyranosides with lead tetraacetate in water was shown to remove carbon atom 3 and form carbonyl groups at carbon atom 2 and 4, producing the two enantiomorphic forms of methoxy-diglycolic aldehyde[4] (II).
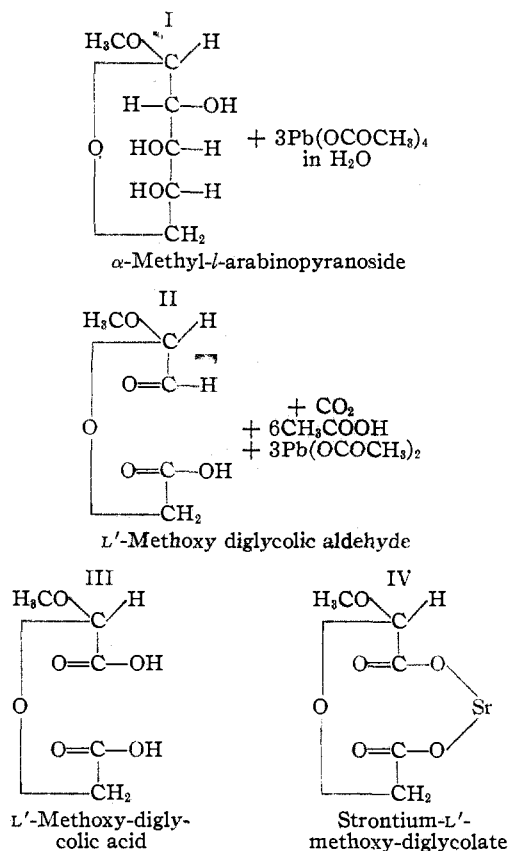
Contrary to previous experience,[1] *three* molecules of lead tetraacetate, instead of two, were required to complete this reaction. In seeking for

(1) Erich Baer, J. M. Grosheintz and H. O. L. Fischer, THIS JOURNAL, **61**, 2607 (1939).

(2) E. L. Jackson and C. S. Hudson, *ibid.*, **59**, 994 (1937).

(3) Compare also W. S. McClenahan and R. C. Hockett, *ibid.*, **60**, 2061 (1938).

(4) The oxidation products are named in accordance with E. L. Jackson and C. S. Hudson, *ibid.*, **59**, 994 (1937), as derivatives of diglycolic aldehyde. Prefixes D' and L' distinguish the configuration of carbon atom 1 in the products from the alpha- and beta-methyl-glycosides, L' signifying the configuration of carbon atom 1 as in alpha-methyl-*l*-arabinopyranoside.

H₃CO $\diagdown$ $_I$ $\diagup$H
C
H—C—OH
HOC—H   + 3Pb(OCOCH₃)₄
O   in H₂O
HOC—H

CH₂

α-Methyl-*l*-arabinopyranoside

H₃CO $\diagdown$ $_{II}$ $\diagup$H
C
O=C—H
                    + CO₂
O   + 6CH₃COOH
                    + 3Pb(OCOCH₃)₂
O=C—OH

CH₂

L'-Methoxy diglycolic aldehyde

H₃CO $\diagdown$ $_{III}$ $\diagup$H   H₃CO $\diagdown$ $_{IV}$ $\diagup$H
C C
O=C—OH   O=C—O
O   O   Sr
O=C—OH   O=C—O

CH₂   CH₂

L'-Methoxy-digly-   Strontium-L'-
colic acid   methoxy-diglycolate

an explanation for this utilization of a third molecule of lead tetraacetate, it was found that one molecule of formic acid in aqueous solution is oxidized by one molecule of lead tetraacetate, yielding one molecule of carbon dioxide.[5] This observation shows that in cases where the velocity of cleavage of the carbon chain between the three adjacent hydroxyl groups is low compared to the rate of oxidation of the formic acid, one must allow for an excess of one mole of lead tetraacetate being used up by the formic acid formed during the reaction.

Further oxidation of the D'- and L'-methoxy-diglycolic aldehydes with bromine water in the presence of strontium carbonate produced the D'- and L'-methoxy-diglycolic acids, the latter being isolated as the crystalline strontium salts. The optical rotations of the starting materials in aqueous solution were $[\alpha]^{20}$D +17.3° for the alpha-methyl-*l*-arabinopyranoside (m. p. 131°)

(5)   It can be assumed that the formic acid is present in its *ortho* form and that the following steps are involved

HC $\diagup$OH   HC $\diagup$OH   O=C $\diagup$OH
   $\diagdown$OH → $\diagdown$O— → $\diagdown$OH
   \OH   \O—
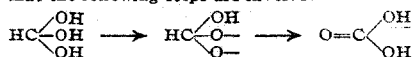
This reaction does not take place in dry organic solvents, or in aqueous solution by means of periodic acid.

and $[\alpha]^{21}$D +246° for the beta-methyl-*l*-arabinopyranoside (m. p. 169–170°). The following rotations for the oxidation products were observed: $[\alpha]^{20}$D +123.2° and $[\alpha]^{23}$D −122.5° for the D'- and L'-methoxy-diglycolic aldehydes (II), $[\alpha]^{20}$D −12.8° and $[\alpha]^{21}$D +12.7° for the D'- and L'-methoxy-diglycolic acids (III); $[\alpha]^{20}$D −56.4° and $[\alpha]^{20}$D +56.4° for the strontium salts of D'- and L'-methoxy-diglycolic acids (IV). The L'-compounds are derived from the alpha-methyl-*l*-arabinopyranoside, the D'-compounds from the beta-methyl-*l*-arabinopyranoside. The optical rotation of each of these compounds checks closely with those obtained by the oxidation of alpha- and beta-methyl-*d*-arabinopyranosides, as recorded by E. L. Jackson and C. S. Hudson.

Experimental

Oxidation of alpha-Methyl-*l*-arabinopyranoside.—A solution of 2.00 g. of alpha-methyl-*l*-arabinoside in 20 cc. of distilled water was poured into 50 cc. of glacial acetic acid[6] containing 13.0 g. of lead tetraacetate, partially undissolved. Within the next six hours 4.0 g. of lead tetraacetate was added in small portions, until the solution turned slightly brown and turbid (=3.2 mole of lead tetraacetate). The solution was then made up to 500.00 cc. with 80 cc. of N sulfuric acid and distilled water. The precipitate of lead sulfate was removed by centrifuging and the content of aldehyde determined according to the method of Willstätter and Schudel. The calcd. yield of L'-methoxy-diglycolic aldehyde is 1.61 g.; found, 1.58 g. = 98% yield. The optical rotation of the solution was α^{23}D −0.39, $c = 0.316$.

The solution was then freed from the slight excess of sulfuric acid with the exact amount of barium acetate and the water and the acetic acid were removed from the dialdehyde by distillation *in vacuo* (bath 35–40°). In order to remove the last traces of acetic acid, the residue was dissolved in 30 cc. of benzene and the solvent evaporated *in vacuo* (bath 35–40°). This operation was repeated twice and the remaining dialdehyde was dried for one hour in high vacuum (40°).

The dialdehyde was then dissolved in 300 cc. of distilled water; 18 g. of strontium carbonate and 8 g. of bromine were added and the mixture was shaken for one hour. After standing at room temperature for an additional sixteen hours, the excess bromine was removed by aeration and the strontium carbonate by filtration. The solution was concentrated and made up to 250.00 cc. The rotation of the strontium L'-methoxy-diglycolate in the solution containing strontium bromide was $[\alpha]^{25}$D +55.1°.

The bromide ions in the solution were removed by shaking with 25 g. of silver carbonate, and the silver ions precipitated by hydrogen sulfide. The solution was concentrated *in vacuo* (45–50°) to about 100 cc., then filtered

(6)   The amount of water and glacial acetic acid can be chosen freely according to the solubility and amount of substance used. Lead tetraacetate can also be added to the aqueous solution of the glycoside in finely powdered form.

and concentrated again to about 10 cc. This liquid was left to evaporate over phosphorus pentoxide for two days and yielded 2.1 g. of crystalline strontium L'-methoxy-diglycolate. After drying the strontium salt over phosphorus pentoxide for six hours at 100° in high vacuum, it showed the optical rotation $[\alpha]^{20}D$ +56.4°.

Anal. Calcd. for $C_5H_6O_6Sr$: C, 24.03; H, 2.40; Sr, 35.01. Found: C, 23.90; H, 2.53; Sr, 34.98.

Oxidation of beta-Methyl-*l*-arabinopyranoside.—The procedure was the same as reported for alpha-methyl-*l*-arabinopyranoside. The optical rotation of the D'-methoxy-diglycolic aldehyde was $[\alpha]^{20}D$ +123.2° $(\alpha^{20}D$ +1.98°; $c = 1.61$, H_2O; tube 1 dm.) and the yield determined by titration according to the method of Willstätter and Schudel was 1.53 g. = 95%. The yield of strontium salt was 71%; $[\alpha]^{20}D$ −56.4° $(\alpha^{20}D$ −1.36°; $c = 2.41$, H_2O; tube 1 dm.) for the anhydrous substance.

Anal. Calcd. for $C_5H_6O_6Sr$: C, 24.03; H, 2.40; Sr, 35.01. Found: C, 23.95; H, 2.55; Sr, 34.96.

Oxidation of Formic Acid.—A roughly 5% aqueous solution of formic acid was prepared and its exact amount of acid determined by titration; 10 cc. of this solution, containing 0.5253 g. of formic acid, was added to 25 cc. of glacial acetic acid and 6 g. of lead tetraacetate in an apparatus suitable for the quantitative determination of carbon dioxide. The mixture was shaken gently and kept at 35°, raising the temperature to 45° within the next half hour, after which time the reaction was completed. In three such experiments 0.4952 g., 0.4843 g., 0.4978 g. of CO_2 were found; yields were 98.8, 96.4 and 99.3%.

Summary

It has been shown that the oxidative cleavage of alpha- and beta-methyl-*l*-arabinopyranosides can be carried out quantitatively in aqueous solution with lead tetraacetate. Three moles of the oxidizing agent, instead of two, are required to complete this reaction. The reason for this excess consumption of reagent is that in aqueous solution the one mole of formic acid formed during the first reaction is oxidized by one mole of lead tetraacetate to one mole of carbon dioxide.[6]

Mechanism of the Reaction between Phthalic Anhydride and an Aminodiol[1]

BY MURRAY M. SPRUNG

Much attention has been devoted recently to the mechanism of polycondensation reactions.[2] Aside from the interesting theoretical deductions to which this work has led, the important practical result is that it is now usually possible to predict whether a condensation reaction will lead to the formation of low molecular weight substances, linear polymers or cross-linked types of resins. The last named are formed, in general, when the initial reactants have higher combined functionalities than 2:2.[2b]

Esterification and amidation reactions conform to these general schemes. Bi-bi-functional esterifications lead to cyclic monomers when rings of five or six members can result; otherwise linear polymers usually are formed. Bi-tri-functional esterifications practically always lead to net-like, cross-linked polymers. As for amidations, Carothers and Berchet[3] found that five and six ring

monomers are formed exclusively, that a seven ring monomer and the corresponding linear polymer appeared simultaneously, and that reactions which might lead to cyclic monomers having eight or more ring atoms led, instead, exclusively to polymers.

Hydroxy amines would be expected to react with dibasic acids in accord with these now well-established principles. An amino-alcohol should give a linear polymeric ester-amide; whereas an aminodiol should give a product having a three dimensional, network structure analogous to that of glyceryl phthalate. This product, furthermore, should show the property of passing suddenly through the sol–gel transformation at a definite, critical stage in the polycondensation reaction.

Preliminary Results.—The reactions of 2-amino-2-methyl-1-propanol with adipic acid, and of 2-amino-2-methyl-1,3-propanediol with succinic, maleic, adipic and sebacic acids gave the results anticipated on the basis of these considerations. In the first case, the product was a thermoplastic resin and apparently a linear polymer. In the latter cases, cross-linked resins were formed which were converted to insoluble, infusible materials when the combined esterification and amidation

(1) Presented at the Boston meeting of the American Chemical Society, September 11–16, 1939.

(2) See, for example, (a) Carothers, THIS JOURNAL, **51**, 2548 (1929); (b) *Trans. Faraday Soc.*, **32**, 39 (1936); (c) Dostal and Raff, *Monatsh.*, **68**, 188 (1936); (d) Flory, THIS JOURNAL, **58**, 1877 (1936); **59**, 466 (1937); (e) Dreher, *Kunststoffe*, **28**, 35 (1938); (f) Stoll and Bouvé, *Helv. Chim. Acta*, **18**, 1087 (1935).

(3) Carothers and Berchet, THIS JOURNAL, **52**, 5289 (1930); see also Carothers, U. S. Patents 2,071,253, 2,130,523, 2,130,947 and 2,130,948 (1937 and 1938).