Oxidation of Carbohydrate Derivatives with Silver Carbonate on Celite. The Degradation of 3-*O*-Methyl-D-glucose

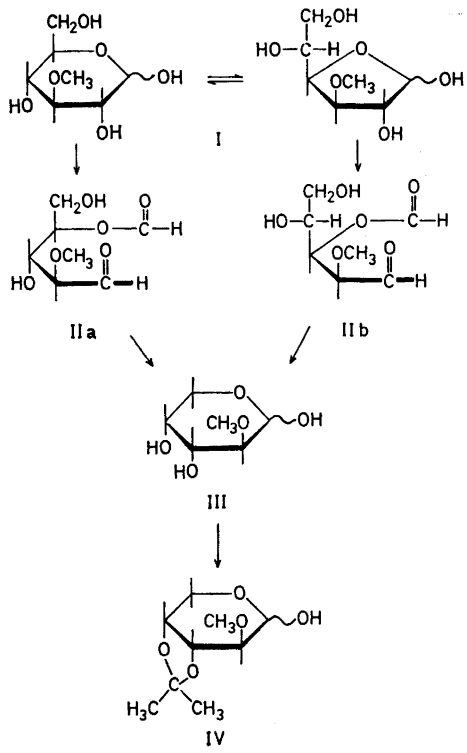
SVEIN MORGENLIE

Department of Chemistry, Agricultural College, N-1432 Vollebekk, Norway

In a previous paper the oxidation with silver carbonate on Celite of some tri- and tetra-*O*-methyl aldoses to the corresponding aldonolactones was reported.[1] It was observed that a 2-*O*-substituent was necessary to prevent degradation. The oxidative degradation of aldoses not substituted in position 2 is now under investigation, and the present paper describes the action of silver carbonate on Celite on 3-*O*-methyl-D-glucose (I).

Methanol was found to be a suitable solvent, and the reaction was complete within 15 – 20 min at 55 – 60°, whereas boiling in benzene solution was needed to bring about oxidation to aldonolactones of 2-*O*-substituted aldoses.[1] Thin layer chromatography of the product mixture showed the presence of three compounds, all moving faster than 3-*O*-methyl-D-glucose (I). The two fastest moving compounds (IIa and IIb) could be visualized with diphenylamine – aniline – phosphoric acid reagent as well as with hydroxylamine – ferric chloride,[2] which gives colour with esters. The third product (III) reacted only with the former reagent. The chloroform-soluble part of the reaction mixture showed a strong infrared absorption at 1723 cm^{-1}, characteristic of formyl esters.[3,4] Hydrolysis of the product mixture in dilute alkaline solution for 30 min at room temperature gave the chromatographically slowest moving compound (III) as the only detectable product, identified as 2-*O*-methyl-D-arabinose through its optical rotation, chromatographical behaviour and conversion to the crystalline 3,4-*O*-isopropylidene derivative (IV).

The initial oxidation products (IIa and IIb) are in light of these facts presumably the 3-*O*- and 4-*O*-formyl derivatives of 2-*O*-methyl-D-arabinose, formed on oxidative cleavage of the 1,2-glycol grouping of the cyclic forms of 3-*O*-methyl-D-glucose(I) as in analogous oxidative degradations



with periodate [5,6] and lead tetraacetate.[3,7] It is not clear whether the oxidation occurs exclusively in cyclic forms. However, the presence of 2-*O*-methyl-D-arabinose before alkaline hydrolysis does not exclude this possibility, since the formyl esters are unstable under the reaction conditions. They were almost completely transformed to the 2-*O*-methyl pentose (III) on prolonged treatment with silver carbonate on Celite in methanol. The 2-*O*-methyl pentose was, on the other hand, stable to the oxidant even in refluxing methanol.

3-*O*-Methyl aldohexoses, obtainable by methylation and hydrolysis of several now easily prepared [8–12] 1,2:5,6- and 1,2:4,6-di-*O*-alkylidene hexoses, are valuable precursors in the synthesis of 2-*O*-methyl pentoses through oxidative degradation.[13–16] Periodate, which is the most usual oxidant in such reactions, suffers from the disadvantage of being able to cleave exocyclic, vicinal diol groupings of the hexofuranose ring present in equilibrium with the pyranose form. Silver carbonate

on Celite has been found to attack 1,2-*O*-isopropylidene-α-D-glucofuranose only to a low degree in methanol at 60°,[17] and the oxidant may possibly be a useful alternative to periodate in the oxidative degradation reactions, particularly in cases where furanose forms are present in considerable amounts.

Experimental. Thin layer chromatography was performed on silica gel in benzene-ethanol 5:2 (v/v) and paper chromatography on Whatman No. 1 paper with the solvent system butanol-pyridine-water 5:3:2. As spray reagents were used diphenylamine-aniline-phosphoric acid,[18] aniline oxalate and hydroxylamine-ferric chloride.[2]

Oxidation of 3-O-methyl-D-glucose (I). A solution of 3-*O*-methyl-D-glucose (I)[19] (200 mg) in methanol (50 ml) was stirred magnetically at 55°, and silver carbonate on Celite[20] (5 g) was added in portions over a period of 15 min. The stirring was continued for further a 5 min period. Thin layer chromatography then showed the presence of three compounds; the two fastest moving could be visualized with diphenylamine–aniline–phosphoric acid reagent as well as with hydroxylamine–ferric chloride, whereas only the former reagent gave colour with the third component. All the starting material had disappeared. The solution was filtered, and a part of it evaporated to a syrup which showed strong infrared absorption at 1723 cm^{-1} ($CHCl_3$). To the methanolic solution was added sodium hydroxide (400 mg) in water (4 ml), and after 30 min the solution was neutralized with Dowex 50 W ion exchange resin. Filtration and evaporation of the solvent gave a syrupy residue which was extracted with ethyl acetate-methanol (4:1, 25 ml). Undissolved material was removed by filtration, and evaporation of the solvent afforded 2-*O*-methyl-D-arabinose (III) as an almost colourless, chromatographically homogeneous syrup (120 mg, 71 % of theoretical), indistinguishable from an authentic sample of 2-*O*-methyl-D-arabinose by paper and thin layer chromatography. $[\alpha]_D^{20} - 90°$ (c 1, water) [lit.[14] – 87°].

3,4-O-Isopropylidene-2-O-methyl-D-arabinose (IV). 2-*O*-Methyl-D-arabinose (III) (20 mg) from the degradation of 3-*O*-methyl-D-glucose by silver carbonate on Celite was treated with trifluoroacetic acid (0.06 ml) in acetone (3 ml) for 70 h. The solution was then poured into saturated, aqueous sodium bicarbonate (10 ml). Evaporation of the acetone and extraction three times of the water solution with chloroform (5 ml portions) gave after evaporation of the solvent and crystallization from benzene 3,4-*O*-isopropylidene-2-*O*-methyl-D-arabinose (IV) (12 mg); m.p. 119–20°, [lit.[14] 121°], $[\alpha]_D^{20} - 125°$ (*c* 0.5, methanol), [lit.[14] – 121°].

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Received September 21, 1971.