[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

AMINOCELLULOSE DERIVATIVES

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The work here presented had two objectives: (a) to introduce an amine function in place of one or more hydroxyl groups in cellulose and (b) to prepare certain cellulose derivatives in which the positions of the substituent groups are known with some degree of certainty. The first of these objectives has been reached by the introduction of phthalimido groups into the cellulose chain equivalent to 0.44 phthalimido groups per anhydro-D-glucose unit of the cellulose. The second objective was attained by the preparation of the following series of derivatives.

6-O-tritylcellulose → 2,3-O-diacetyl-6-O-tritylcellulose →
2,3-di-O-acetylcellulose → 2,3-di-O-acetyl-6-O-tosylcellulose →
2,3-di-O-acetyl-6-deoxy-6-iodocellulose.

1. INTRODUCTION OF AMINO GROUPS INTO THE CELLULOSE CHAIN

Attempts to introduce a primary amino group into cellulose have been only slightly successful. Alkylaminocelluloses, however, were prepared by Haskins (1) by the action of primary or secondary amines on tosylated cellulose derivatives. The more satisfactory action of primary and secondary amines as compared to that of ammonia appears to be due to the tendency of the latter to react with two or more tosyl groups, thereby cross-linking the cellulose chains.

By treating a tosylated cellulose acetate (1.85 acetyl groups and 0.43 tosyl groups per anhydro-D-glucose unit) with a solution of potassium phthalimide in acetamide we have been able to replace the tosyl groups stoichiometrically by phthalimido groups. Attempts to remove the phthalic acid residues were not successful.

Treatment of a 2,3-di-O-acetyl-6-O-tosylcellulose in a like manner gave about 25% replacement of the tosyl groups, while treatment of 2,3-di-O-acetyl-6-O-tosylcellulose with *n*-butylamine gave 87% replacement.

2. PREPARATION OF CELLULOSE DERIVATIVES WITH SUBSTITUENTS IN KNOWN POSITIONS

When cellulose is treated with triphenylmethyl chloride (commonly called "trityl" chloride) in anhydrous pyridine a triphenylmethyl ether is formed (2, 3). The rate of tritylation of the primary hydroxyl group is so much greater than that of the secondary hydroxyl group (4) that tritylation up to one group per anhydro-D-glucose unit is essentially primary and the monosubstituted ether may be assumed to be 6-trityl.

A quantitative acetylation of monotritylcellulose was effected by Hearon and co-workers (4) to yield the 2,3-di-O-acetyl-6-O-tritylcellulose and the product was detritylated to yield 2,3-diacetylcellulose.

In our work a 2,3-di-O-acetylcellulose was prepared by the above method. This product was tosylated by the method of Purves and Cramer (5). The resulting product was essentially a 2,3-di-O-acetyl-6-O-tosylcellulose. Proof that this was its structure lies in the fact that treatment with sodium iodide according to the method of Purves and Mahoney (6) gave 100% replacement of the tosyloxy group by iodine.

When the 2,3-di-O-acetyl-6-O-tosylcellulose was treated with isobutylamine a derivative was obtained which contained 0.87 isobutylamino group for each anhydro-D-glucose residue. Treatment with potassium phthalimide gave a derivative containing 0.25 phthalimido groups for each anhydro-D-glucose residue.

EXPERIMENTAL

Tosylation of cellulose acetate. The procedure of Purves and Cramer (5) was used. Two separate preparations gave analyses corresponding to 1.82 acetyl groups with 0.43 tosyl groups and 1.60 acetyl groups with 0.46 tosyl groups, respectively.

Preparation of N-phthalimidocellulose acetate. To 29.9 g. of a tosylated cellulose acetate (analysis 25.69% acetyl, 4.54% S) dissolved in 1070 ml. of anhydrous pyridine, in a 3-liter, 3-necked flask equipped with a reflux condenser, drying tube, stirrer, and thermometer and fitted with a heating mantle, was added 19.0 g. of potassium phthalimide (a 2.5 *molar* quantity based on the tosyl content) dissolved in 840 g. of acetamide at 50°. After heating the homogeneous reaction mixture for three hours at 85–90°, it was precipitated into four liters of 95% alcohol. A small precipitate (2.3 g.) which formed was extracted with ethanol and dried. The alcoholic mother liquor was poured into 6 liters of water. This yielded a further precipitate (24.1 g.) which was washed and dried. Analysis of the small, alcohol-insoluble precipitate showed 18.18% acetyl, 1.42% S, and 0.49% N equivalent to 0.96 acetyl group, 0.1 tosyl group, and 0.08 phthalimido group. It would appear to be a hydrolysis product. The major fraction showed 20.66% acetyl, 0.75% S, and 2.16% N, corresponding to 1.36 acetyl groups, 0.06 tosyl group, and 0.438 phthalimido group per anydro-D-glucose unit.

Tritylation of cellulose. Cellulose regenerated from cellulose acetate was used as starting material and the method of Hearon and associates (4) was applied for the tritylation. Analysis showed an average tritanol content of 65.54% corresponding to 1.02 trityl groups per anhydro-D-glucose unit.

Acetylation of monotritylcellulose. The O-tritylcellulose was acetylated according to the procedure of Hearon and associates (4). Analysis of the product showed 17.27% acetyl and 51.42% tritanol corresponding to 1.02 trityl groups and 1.98 acetyl groups per anhydro-D-glucose unit.

Preparation of 2,3-di-O-acetylcellulose. Detritylation of the mono-O-tosyl-, di-O-acetylcellulose by this method of Hearon and associates (4) yielded a 2,3-di-O-acetate of cellulose whose analysis showed 35.68% acetyl corresponding to 2.08 acetyl groups per anhydro-D-glucose unit.

Preparation of 2,3-di-O-acetyl-6-O-tosylcellulose. Tosylation of the 2,3-di-O-acetate of cellulose by the method of Purves and Cramer (5) yielded a derivative containing 22.5% acetyl with 7.64% S, corresponding to 0.94 tosyl group and 2.06 acetyl groups per anhydro-D-glucose unit.

Iodination of 2,3-di-O-acetyl-6-tosylcellulose. For this step the procedure of Purves and Mahoney (6) was used. The product showed 35.22% iodine and 0.15% S, corresponding to 0.02 tosyl group, 1.99 acetyl groups and 0.99 iodine atom per anhydro-D-glucose unit.

Amination of 2,3-di-O-acetyl-6-O-tosylcellulose. To 1.0 g. 2,3-di-O-acetyl-6-O-tosylcellulose, 40 ml. of isobutylamine was added. The cellulose derivative dissolved in this solvent within 24 hours at 25°. After seven days at 25° the solution was filtered, refluxed for 15 hours at 68°, and coagulated by pouring it into 1 liter of commercial ether. The coagulated product was filtered on a sintered glass funnel and was washed once with ether, four times with cold water, and twice with boiling water. After drying in a vacuum over Drierite, 0.3 g. of alkylaminated product was obtained. Analysis showed 5.62% N and 5.92% acetyl with only a trace of sulfur. This is in agreement with 0.87 isobutylamino groups per anhydro-D-glucose unit.

Reaction of 2,3-di-O-acetyl-6-O-tosylcellulose with potassium phthalimide. The process described in the second section of the experimental portion when applied to the above product yielded a phthalimido derivative whose analysis showed 1.4% N and 25.35% acetyl in agreement with 0.25 N-phthalimido and 1.47 acetyl groups per anhydro-D-glucose unit.

SUMMARY

1. A phthalimide derivative of cellulose has been prepared, containing approximately one-half phthalimido group per anhydro-D-glucose unit of the cellulose.

2. A 2,3-di-O-acetyl-6-O-tosylcellulose has been prepared in which the location of the various groups is known with some degree of certainty.

3. Partial replacement of the tosyloxy groups in the above mentioned derivatives by isobutylamino groups and by phthalimido groups has been achieved.

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