SYNTHESIS OF 2, 3-ANHYDRO-6,O- TRITYLCELLULOSE

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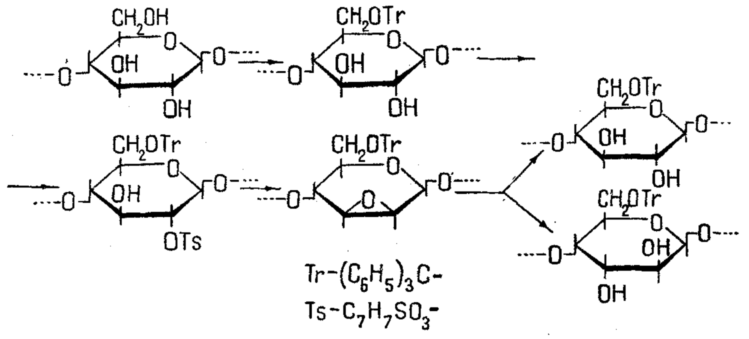
The formation of anhydro rings in macromolecular polysaccharides takes place predominantly under the action of alkalis on tosyl, mesyl, and sulfo esters of the polysaccharides.

The synthesis of 2, 3-anhydro derivatives of tritylcellulose has previously been effected [1] by the action of a solution of sodium methoxide or caustic potash in absolute methanol on trityl-cellulose tosylate. In addition to the formation of 2, 3-anhydro rings in the cellulose macromolecule, some ring opening with the introduction of a methoxy group takes place. At the same time, side reactions occur leading to the appearance of carbonyl groups and double bonds, in the elementary unit of the macromolecule, which makes it impossible to synthesize the product in the pure state.

The present paper gives the results of an investigation of the possibility of synthesizing 2, 3-anhydro derivatives of cellulose and subsequently opening the α-oxide rings with the formation of a mixed polysaccharide by the action of aqueous solutions of alkali on tritylcellulose tosylate by the following route:



Tritylcellulose tosylate was saponified by treatment with boiling aqueous solutions of caustic soda of various concentrations. The reaction was carried out in a current of argon in a heterogeneous medium. The sulfur contents of the reaction products were determined (table).

NaOH, %	Sulfur content (%) of tritylcellulose tosylate after treatment with an aqueous solution of caustic soda for varying lengths of time.				
	10 hr	15 hr	30 hr	40 hr	60 hr
6	2, 65	2, 11	1, 68	1, 61	1, 35
10	3, 56	2, 07	1, 58	1, 10	1, 04
15	2, 90	1, 42	1, 12	0, 94	0, 89

Note. The initial tritylcellulose tosylate $(OTs)_{0.96}$ had the composition $C_6H_7O_2(OH)_{1.10}(OTr)_{1.04}(OTs)_{0.96}$, and a sulfur content of 5.5%.

As can be seen, complete elimination of the tosyl groups was not achieved even with very prolonged treatment of the ester, which agrees with the results obtained by other authors [2, 3]. With increasing concentration of caustic soda in the solution, the amount of sulfur in the saponification products fell. The minimum tosyl group content of the products of the alkaline treatment of tritylcellulose tosylate was obtained as a result of the action of a 15% aqueous solution of caustic soda for 60 hr.

By analogy with the results obtained earlier, it might be expected that the detosylation of tritylcellulose tosylate would take place with the formation of 2, 3-anhydro rings whose opening would subsequently lead to the formation of glucopyranose and altropyranose elementary units in the macromolecule. Under these conditions side reactions causing the appearance of double bonds and carbonyl groups are possible [1].

In order to answer this question, the products of the detosylation of a tritylcellulose tosylate of the composition $C_6H_7O_2(OH)_{0.98}(OTr)_{1.04}(OTs)_{0.98}$ with a 15% aqueous solution of caustic soda for 60 hr were investigated. In one case the reaction product contained 0.89% of sulfur (I) and in another case 0.66%(II).

To determine the 2,3-anhydro ring content quantitatively, part of the product was treated with a solution of sodium methoxide in absolute methanol at 120° for 48 hr. Under these conditions complete opening of the 2, 3-anhydro rings took place [1]. The methoxy group content of the products obtained was determined: 1.98% of OCH_3 was found in product (I) and 2.33% in (II), which showed the formation of 0.26 and 0.32 anhydro rings per elementary unit of the macromolecule, respectively.

In order to discover the possibility of the occurrence of side reactions in the saponification of the tosyl groups in the tritylcellulose tosylate, the reaction products were brominated [5], and the oximes were synthesized [4]. The nitrogen content of the oxime products was determined by the Dumas method: 0.94% was found in product (I) and 0.88% in product (II), the figures for the initial tritylcellulose tosylate after oxime formation being 0.49-0.52%. Consequently, during oxime formation from tritylcellulose tosylates saponified by aqueous solutions of alkalis, the carbonyl group content increases insignificantly, which indicates the absence of side reactions leading to the formation of such groups.

The determination of the bromine number showed that there were no double bonds in products (I) and (II). Thus, no side reactions take place under the detosylation conditions selected.

To determine the possibility of the opening of the 2, 3-anhydro rings during the saponification of the tritylcellulose tosylate requires the preliminary detritylation of this compound. An investigation of the detritylation of product (II) showed that the trityl groups can be eliminated completely by treating the compound with a 0.2% solution of hydrogen chloride in chloroform for 24 hr.

After detritylation, the products were subjected to complete hydrolysis or methanolysis. The resulting mixture of sugars was investigated by paper chromatography. If detosylation of the tritylcellulose tosylate had taken place with the intermediate formation of 2, 3-anhydro rings and their subsequent opening, the hydrolyzate should have contained altrose – more accurately < 1, 5>, < 1, 6 >-anhydroaltrose (altrosan), since in an acid medium altrose is readily converted into altrosan [6]. In addition to the hydrolyzate, solutions of reference samples of glucose and altrosan* were deposited on the chromatogram; none of the latter was found.

The complete methanolysis of the polysaccharide obtained was carried out by the action of a solution of hydrogen chloride in methanol on the product of the saponification of the tritylcellulose tosylate. Chromatography of the methylglycosides with reference samples (solutions of methyl α-D-glucoside and methyl α-D-altroside) showed that there was no methyl α-D-altroside in the methanolysis products.

Consequently, when tritylcellulose tosylate is detosylated with aqueous solutions of alkalis, there is no opening of the 2, 3-anhydro rings and no formation of a mixed polysaccharide.

To study the possibility of the opening of the 2, 3-anhydro rings on alkaline treatment without a change of configuration, we studied the stability of the 2, 3-anhydro rings in 2, 3-anhydro-6-O-tritylcellulose under the action of a 6% aqueous solution of NaOH. Even on prolonged treatment (for 60 hr) with the boiling solution the amount of 2,3-anhydro rings did not change.

The results obtained give grounds for assuming that the splitting off of the tosyl groups from the tritylcellulose tosylate takes place as a result of two chemical reactions: saponification (with the regeneration of the OH groups and the restoration of the initial configuration of the glucopyranose link) and the formation of 2, 3-anhydro rings, which are not opened under the conditions mentioned.

Experimental**

Saponification of tritylcellulose tosylates with aqueous solutions of caustic soda. 1 g of tritylcellulose tosylate was treated with a 6, 10, or 15% solution of caustic soda (in a ratio of 50 : 1) at the boiling point of the solution in a current of argon for various times. After the end of the reaction, the products were washed with distilled water to neutrality and dried under vacuum over P_2O_5. The sulfur content of the product was determined.

Detritylation of the saponification products of tritylcellulose tosylate. 1 g of product was treated at room temperature for 24 hr with a mixture of 30 ml of chloroform and 10 ml of chloroform saturated with hydrogen chloride at –7°C. After the completion of the detritylation, the product was precipitated in methanol, extracted with methanol, washed with water, and dried under vacuum over P_2O_5.

Hydrolysis of the products of the saponification of tritylcellulose tosylate. A 20-ml tube was charged with 60 mg of polysaccharide and with 0.6 ml of 72% sulfuric acid at 0°C, and the mixture was left for 1 hr at 0°C . Then 6 ml of cold water was added and hydrolysis was carried out at 100°C in the sealed tube for 18-20 hr.

Methanolysis of the products of the saponification of the tritylcellulose tosylate. A 10-ml tube was charged with 60 mg of polysaccharide and 4 ml of a 5% methanolic solution of hydrogen chloride. Methanolysis at 120°C was carried out for 18 hr in the sealed tube. After the end of the methanolysis, the tube was opened and the contents were filtered

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through a No. 4 filter and neutralized with silver carbonate. The solution was centrifuged and the residue of silver chloride was washed several times with distilled water. The solution and the wash-waters were evaporated under vacuum. The resulting syrup was analyzed by paper chromatography.

Chromatographic separation of the mixture of monosaccharides. The mixture of monosaccharides obtained by hydrolysis was chromatographed in the ethyl acetate–pyridine–water (2:1:2) system and the methanolysis products in the butan-1-ol-ethanol-water (40:11:19) system by the usual method [7]. The spots were shown up with silver nitrate.

Summary

1. The possibility of obtaining 2, 3-anhydro derivatives of cellulose by the action of aqueous solutions of alkalis on tritylcellulose tosylate has been investigated.

2. The splitting off of the tosyl groups when tritylcellulose tosylate is treated with aqueous solutions of alkalis takes place mainly with the saponification of the tosyl groups and the formation of elementary glucopyranose units, and also with the formation of 2,3-anhydro rings. Under these conditions no side reactions take place.

REFERENCES

1. G. N. Smirnova, A. I. Polyakov, and Z. A. Rogovin, Vysokomol. soed., 7, 972, 1965.
2. Hess and Ljubitsch, Ann., 62, 509, 1933.
3. E. D. Kaverzneva, V. I. Ivanova, and A. S. Salova, Izv. AN SSSR, OKhN, no. 4, 369, 1949.
4. E. N. Novikova and L. N. Petrov, ZhPKh, 23, no. 12, 1336, 1956.
5. I. P. Losev and O. Ya. Fedotova, Practical High Polymer Chemistry [in Russian], Moscow, 84, 1959.
6. A. Rosenfeld, N. K. Richtmyer and C. H. Hudson, J. Am. Chem. Soc., 70, 2201, 1948.
7. Yu. A. Zhdanov, R. N. Dorofeenko, and G. A. Korol'chenko, Practical Carbohydrate Chemistry [in Russian], 112, 1963.

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