SYNTHESIS OF 3, 6-ANHYDROCELLULOSE BY THE SAPONIFICATION OF 6-O-TOSYL-2, 3-DI-O-ACETYLCELLULOSE

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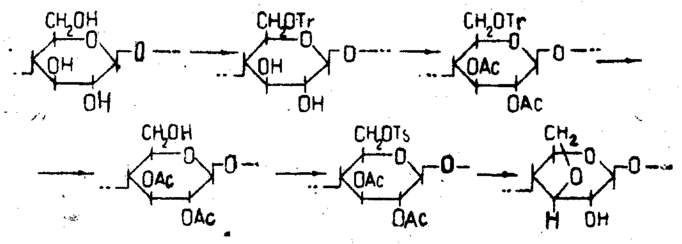
We have previously [1] reported the synthesis of 3, 6-anhydrocellulose by the elimination of a tosyl group in cellulose monotosylate by the action of alcoholic solutions of alkali. However, this method for the synthesis of 3, 6-anhydro derivatives of cellulose takes place with the simultaneous formation of 2, 3-anhydro rings because of the elimination of tosyl groups located on C_2 or C_3, which naturally complicates the analysis of the results obtained.

The present paper gives the results of the synthesis of 3, 6-anhydro derivatives of cellulose by a route which must exclude the possibility of the formation of α-oxide rings, nameless the alkaline saponification of 6-O-tosyl-2, 3-di-O-acetylcellulose:



where Tr = trityl (triphenylmethyl), Ts = tosyl (p-toluenesulfonyl), and Ac = acetyl.

We used tritylation for the selective blocking of the hydroxy groups at C_6. The subsequent elimination of the trityl groups can be carried out under comparatively mild conditions [2, 3].

The trityl ether of cellulose (TEC) was obtained by Helferich's method [4] by the action of triphenylchloromethane in absolute pyridine on undried cellulose regenerated from viscose solution. The preparations of TEC contained 63.3–65.9% of triphenylcarbinol (TPC), which corresponded to a γ value of 96–106 with respect to trityl groups.

The acetylation of tritylcellulose with acetic anhydride in the presence of pyridine has been described [4]. The maximum figure for acetyl groups was about 125. Sakurada and Kitabatake [5] and Makarova-Zemlyanskaya [6] have been able to introduce up to 1.5 acetyl groups per elementary unit into TEC under milder conditions.

Table 1

Influence of the Duration of Acetylation on the Composition of 6-O-Trityl-2, 3-di-O-acetylcellulose*

Time, hr	Content of TPC, %	γ value with respect to trityl groups	Content of bound CH_3COOH, %	γ value with respect to acetyl groups
70	47,2	79	23,20	163
91	52.65	93	22,40	170
115	51,30	99	22,10	175
220	43,85	78	25.90	186

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*Degree of substitution of the initial TEC (γ value), 96.

By increasing the time of acetylation to 250 hr we obtained a product with a higher γ value with respect to acetyl groups, nearly 200. The content of TPC remained constant. Increasing the time of acetylation above 50 hr led to a very slow increase in the amount of acetic acid bound.

The samples of tritylcellulose acetate obtained were purified by reprecipitation from pyridine solutions poured into methanol. To investigate the possibility of increasing the rate of acetylation of TEC, we acetylated it directly after synthesis without previous precipitation and drying (Table 1). The results show that the rate of acetylation did not increase under these conditions.

The subsequent stage in the process of preparing 3, 6-anhydrocellulose was the splitting off of the trityl groups (see scheme). The detritylation of tritylcellulose acetate was carried out by Helferich and Koester's method [4], by treating it with chloroform saturated at room temperature with hydrogen chloride (Table 2). Thus, on detritylation the trityl groups must split off completely without an appreciable change in the degree of substitution with respect to acetyl groups.

Table 2

Composition of the 2, 3-Di-O-acetylcellulose

6-O-Trityl-2, 3-di-O-acetylcellulose				2, 3-Di-O-acetylcellulose			
TPC, %	γ value with respect to trityl groups	Content of bound CH_3COOH, %	γ value with respect to acetyl groups	TPC, %	γ value with respect to trityl groups	Content of bound CH_3COOH, %	γ value with respect to acetyl groups
52.65	93	22.4	170	0	0	42.35	162
47.20	79	23.2	165	0	0	42.51	163
51.30	99	22.1	175	0	0	44.4	176
43.85	78	25.9	186	0	0	47.0	189

The 2, 3-di-O-acetylcellulose obtained was subjected to tosylation by Hess's method [7] by the action of a solution of p-toluenesulfonyl chloride in absolute pyridine (Table 3). It can be seen from Table 3 that the maximum degree of substitution of the 6-O-tosyl-2, 3-di-O-acetylcellulose with respect to tosyl groups is approximately 75. When the time of the reaction was increased, the content of tosyl groups underwent practically no change while the amount of acetyl groups decreased very slightly.

Table 3

Composition of the Products of the Tosylation of 2, 3-Di-O-acetylcellulose

Experiment no.	Composition of the 6-O-trityl-2, 3-di-O-acetylcellulose		Duration of tosylation, hr	Composition of the 6-O-tosyl-2, 3-di-O-acetyl-cellulose			
	γ value with respect to						
	trityl groups	acetyl groups		sulfur content, %	γ value with respect to tosyl groups	Content of bound CH_3COOH, %	γ value with respect to acetyl groups
2	93	170	45	6.83	75	30.0	176
3	79	163	50	6.81	74	29.2	169
5	99	175	57	6.83	75	30.4	176

3, 6-Anhydrocellulose was synthesized by the saponification of 6-O-tosyl-2, 3-di-O-acetylcellulose with a 10% solution of caustic potash in methanol at the boiling point of the solution for 10 hr. The treatment of the 6-O-tosyl-2, 3-di-O-acetylcellulose with the alcoholic solution of alkali led to the complete elimination of the tosyl and the acetyl groups.

The splitting off of the tosyl groups from 6-O-tosyl-2, 3-di-O-acetylcellulose under the conditions that we used must be accompanied by the formation of 3, 6-anhydro rings. The elementary compositions and contents of methoxy groups were determined for the products of the saponification of 6-O-tosyl-2, 3-di-O-acetylcellulose.

Found, %: C 48. 43; H 5.80 Calculated, %, for 3, 6-anhydrocellulose of composition $C_6H_7O_2(O)_{0.84}(OH)_{1.68}(OCH_3)^{*}_{0.17}$, %: C 48; H 5. 60.

Found, %: C 46. 15; H 6. 13. Calculated, %, for 3, 6-anhydrocellulose of the composition $C_6H_7O_2(O)_{0.34}(OH)_{2.32}(OCH_3)_{0.152}$, %: C 46. 20; H 5. 98.

A comparison of the results of elemental analysis with the calculated figures permits the preliminary conclusion that the saponification of 6-O-tosyl-2, 3-di-O-acetylcellulose gives rise to a quantitative formation of 3, 6-anhydro rings.

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[*] The formula for the 3, 6-anhydrocellulose was drawn up on the basis that the splitting off of all the tosyl groups took place with the formation of 3, 6-anhydro rings and the introduction of an $-OCH_3$ group is associated with the opening of the pyranose ring by the rupture of the <1, 5> acetal bond in the bicyclic system [1].

To prove the structure of the anhydro derivative of cellulose obtained, samples of 3, 6-anhydrocellulose were subjected to acetylation with acetic anhydride in the presence of perchloric acid and were nitrated [8], oxidized with periodate [9], and studied by IR spectroscopy [10] (Table 4).

Table 4

Results of the Acetylation, Periodate Oxidation, and Nitration of Samples of 3, 6-Anhydrocellulose

6-O-Tosyl-2, 3-di-O-acetylcellulose		3, 6-Anhydrocellulose*							
γ value with respect to		content of OCH_3 groups, %	periodate oxidation			acetylation		nitration	
tosyl groups	acetyl groups		consumption of HIO_4 in oxidation, g-mole	A	B	content of bound CH_3COOH groups, %	B	nitrogen content, %	B
36	176	2.65	$39 \cdot 10^{-5}$	65	35	57.10	34	12.3	37
36	175	2,68	$37 \cdot 10^{-5}$	66	34	—	—	12.8	28
36	161	3,63	$41 \cdot 10^{-5}$	59	41	53.5	37	12,4	36
73	208	2.83	$145 \cdot 10^{-5}$	35	65	—	—	9.95	72

*All the samples of 3, 6-anhydrocellulose were free from tosyl and acetyl groups. A) number of oxidized units per 100 elementary units; B) number of 3, 6-anhydro rings per 100 elementary units.

The data given in Table 4 show the presence in the cellulose of 3, 6-anhydro rings whose content corresponds to the number of tosyl groups in the initial 6-O-tosyl-2, 3-di-O-acetylcellulose.

The presence of 3, 6-anhydro rings in the products of the saponification of 6-O-tosyl-2, 3-di-O-acetylcellulose was also shown by IR spectroscopy [10]. The spectrum of 3, 6-anhydrocellulose exhibited absorption bands at 920, 840, and 800 cm^{-1} which are characteristic for hydrofuran rings.

Experimental

Moist cellulose was preliminarily pressed out and treated several times with methanol and then with absolute pyridine which was changed every 24 hr for 2–3 weeks.

The tritylation of the cellulose was carried out by a published method [4, 11].

The acetylation of the 6-O-tritylcellulose with acetic anhydride in pyridine was carried out by the procedure given by Shorygin and Makarova-Zemlyaskaya [6].

The detritylation of the 6-O-trityl-2, 3-di-O-acetylcellulose was carried out as follows: at room temperature, 1 g of tritylcellulose acetate was treated for 24 hr with continuous shaking with a mixture of 30 ml of ordinary chloroform and 10 ml of chloroform saturated with hydrogen chloride at the same temperature.

The tosylation of the 2, 3-di-O-acetylcellulose was effected by Hess's method [7].

The saponification of the 6-O-tosyl-2, 3-di-O-acetylcellulose was carried out by boiling it with a 10% solution of caustic potash in absolute methanol for 10–12 hr at a bath ratio of 20.

Summary

1. Derivatives of cellulose containing 3, 6-anhydro rings have been synthesized by the following route: cellulose → 6-O-tritylcellulose → 6-O-trityl-2, 3-di-O-acetylcellulose → 2, 3-di-O-acetylcellulose → 6-O-tosyl-2, 3-di-O-acetylcellulose → 3, 6-anhydrocellulose.

2. The composition of the 3, 6-anhydrocellulose has been studied by exhaustive acetylation, nitration, and periodate oxidation, and also by IR spectroscopy.

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