

Preparation of *O*-(3-azido-2-hydroxypropyl)cellulose and its photolysis to *O*-(2-formyl-2-hydroxyethyl)cellulose

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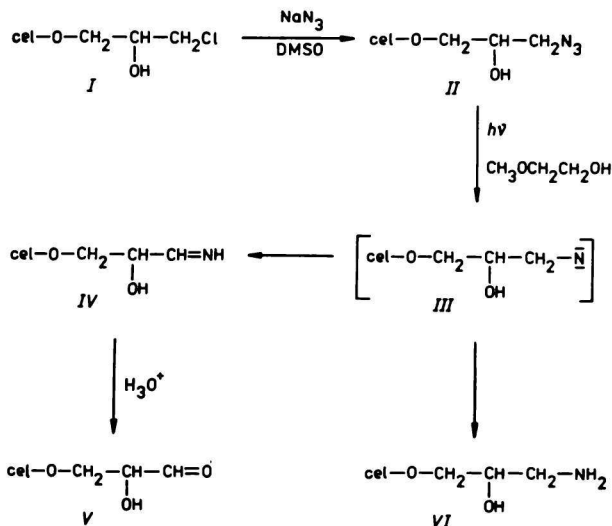
O-(3-Azido-2-hydroxypropyl)cellulose has been prepared by the reaction of *O*-(3-chloro-2-hydroxypropyl)cellulose with sodium azide in dimethyl sulfoxide. Photolysis of this compound in 2-methoxyethanol and subsequent acid hydrolysis afforded *O*-(2-formyl-2-hydroxyethyl)cellulose.

Посредством реакции *O*-(3-хлор-2-гидроксипропил)целлюлозы с азидом натрия в диметилсульфоксиде была получена *O*-(3-азидо-2-гидроксипропил)целлюлоза, из которой в результате фотолиза в 2-метоксиэтаноле и последующего кислого гидролиза образовалась *O*-(2-формил-2-гидроксиэтил)целлюлоза.

It is known that azidomethyl derivatives are suitable precursors for photolytic preparation of aldimine derivatives [1] which on acid hydrolysis release the respective aldehydes. Horton *et al.* [2] described the preparation of 6-aldehydocellulose by photolysis of 6-azido-6-deoxycellulose which was obtained from 6-chloro-6-deoxycellulose. We followed up the same way in preparation of a further substitution aldehyde derivative of cellulose, *i.e.* *O*-(2-formyl-2-hydroxyethyl)cellulose (V), from the starting *O*-(3-chloro-2-hydroxypropyl)cellulose (I) with purpose to complete the series of substituted aldehyde derivatives of cellulose prepared so far [3—5].

The starting derivative *I* was prepared by the procedure described earlier [6]. By treatment of *I* with sodium azide (Scheme 1) in dimethyl sulfoxide at 100 °C practically quantitative replacement (92 %) of chlorine with azido group has been achieved within 3 h. *O*-(3-Azido-2-hydroxypropyl)cellulose (II), not containing residual chlorine, was obtained in the form of white floccules after diluting the gel-like reaction mixture with water and precipitation with acetone. The rate of conversion of *I* to *II* was lower in water, at maintaining the other reaction conditions, where gel formation in the reaction mixture was not observed. Within the same time only 71 % chlorine was replaced probably due to worse accessibility of reaction centres in the unswollen cellulose derivative. When comparing the conversion of *I* to *II* with that of 6-chloro-6-deoxy- to 6-azido-6-deoxycellulose [2] it can be seen that in our case the desired conversion was achieved in much

shorter time due to the reactive α -halohydrine grouping. The IR spectrum of the derivative *II* revealed at $\bar{\nu} = 2100 \text{ cm}^{-1}$ a strong absorption band characteristic of the azido group.



Scheme 1

Photolysis of the azido derivative *II* in 2-methoxyethanol was carried out under heterogeneous conditions. Quantitative decomposition of the azido derivative was achieved at 45–50 °C within 2 h, as proved by complete disappearance of the azido band in the IR spectrum of the product. The obtained aldimine derivative *IV*, which is assumed to be formed [1] by rearrangement of α -proton of the alkylnitrene derivative *III*, was hydrolyzed in the next step with diluted acetic acid. The prepared aldehyde derivative *V*, containing residual nitrogen (15 %) unre-movable on acid hydrolysis, showed in the IR spectrum a weak absorption band at $\bar{\nu} = 1720 \text{ cm}^{-1}$, characteristic of aliphatic aldehydes. The residual nitrogen is probably of amino nature since, beside isomerization of methylnitrene group to aldimine, always proceeds a competitive splitting of hydrogen atoms of the solvent by the nitrene intermediate to give amine [1], in our case probably the derivative *VI*.

The degree of substitution (DS) by 2-formyl-2-hydroxyethyl group in the prepared aldehyde derivative *V* was determined by the 4-nitrophenylhydrazine method [4]. Subtracting the residual nitrogen, which remained in the derivative *V* after hydrolysis of the aldimine *IV*, the conversion of the azide *II* to aldimine *IV* achieved on photolysis was calculated to be 50 %. Since the derivative *V* is actually a 3-*O*-alkyl substituted DL-glyceraldehyde, there was a possibility of its conversion

to the corresponding 4-nitrophenylosazone. This possibility was excluded by additional experiment where DL-glyceraldehyde with excess 4-nitrophenylhydrazine (3 mol) afforded at the same conditions as in [4] only 4-nitrophenylhydrazone of DL-glyceraldehyde.

Experimental

O-(3-Azido-2-hydroxypropyl)cellulose (II)

The mixture of *I* [6] (0.5 g; $w_{\text{chlorine}} = 5.40\%$, $DS = 0.29$), sodium azide (0.65 g), and dimethyl sulfoxide (10 cm³) was stirred and heated at 100 °C for 3 h. The reaction mixture was poured into water (100 cm³) and after addition of acetone (150 cm³) and stirring a white floccule-like compound precipitated within some minutes. After 1 h the solid phase was decanted five times with the mixture of water—acetone (volume ratio = 3:1). Then the solid phase was filtered off, washed with methanol, and dried with ether to give *II* (0.5 g; IR: $\tilde{\nu} = 2100\text{ cm}^{-1}$ (azido group), $w_{\text{chlorine}} = 0.0\%$, $w_{\text{nitrogen}} = 5.88\%$, $DS = 0.26$).

At the same conditions, but using water (10 cm³) instead of dimethyl sulfoxide, a mixture of the derivatives *II* and *I* was obtained (0.5 g; $w_{\text{nitrogen}} = 4.83\%$, $DS = 0.21$, $w_{\text{chlorine}} = 1.56\%$, $DS = 0.08$) after filtration, washing of the solid phase with water and methanol, and drying with ether.

Photolysis of *O*-(3-azido-2-hydroxypropyl)cellulose (II)

The mixture of *II* (0.1 g; prepared in dimethyl sulfoxide) and 2-methoxyethanol (25 cm³), vigorously stirred under nitrogen, was irradiated in a quartz flask with a high-pressure mercury vapour lamp (Tesla RVK 125 W) of the combined irradiator Sirius (Chirana) at 45—50 °C for 24 h (until the band at $\tilde{\nu} = 2100\text{ cm}^{-1}$ belonging to azido group vanished in the IR spectrum). During photolysis the whole equipment was wrapped up in aluminium foil. The solid phase was then filtered off and washed with methanol thoroughly. A portion of the sample (ca. 4/5, the remaining part was used to determine the aldehyde groups according to [4]) was added to 5 % acetic acid (5 cm³) and the suspension was stirred at room temperature for 16 h. After filtration, washing with water to neutral reaction and drying with methanol and ether, a light yellow compound *V* (IR: $\tilde{\nu} = 1720\text{ cm}^{-1}$ (aldehyde group), $w_{\text{nitrogen}} = 0.88\%$) was obtained. The reaction with 4-nitrophenylhydrazine [4] afforded the 4-nitrophenylhydrazone of the derivative *V* ($w_{\text{nitrogen}} = 3.85\%$), which after subtraction of the residual nitrogen in *V*, corresponded to DS by 2-formyl-2-hydroxyethyl group 0.13.

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