

# PREPARATION OF 5, 6-CELLULOSEEN FROM CELLULOSE NITRATE OF LOW DEGREE OF SUBSTITUTION (D.S.)

W. B. ACHWAL AND S. D. DESHPANDE  
Department of Chemical Technology, University of Bombay

## ABSTRACT

5, 6-Celluloseen of a high degree of unsaturation has been prepared starting from cellulose nitrate containing 7.2% nitrogen, by a series of reactions involving iodination and dehydroiodination. The product obtained was found to be a mixed polysaccharide containing 5, 6-glucoseen, 3, 6-anhydro-D-glucose and D-glucose units similar to the product from cellulose nitrate of high D.S. Determination of free hydroxyl groups in celluloseen is not possible by acetylation as the double-bond takes part in reactions depending upon the conditions of acetylation. The above starting material is preferable in view of the safe handling as well as easier isolation of intermediate compounds.

**I**NTRODUCTION of new types of functional groups into cellulose macromolecule constitutes one of the most interesting and promising trends in modifying the properties of cellulose. The presence of unsaturation in the basic unit of cellulose macromolecule would offer the possibility of attaching new groups directly to the pyranose ring of cellulose. Preparation of such a cellulose derivative containing unsaturation, e.g., 5,6-celluloseen and some chemical transformations of double bond by hydrogenation and radical addition reactions, have been recently carried out.<sup>1,2</sup>

5, 6-Celluloseen prepared from cellulose tosylate as a starting material contains tosylate residues which cannot be easily removed without loss of unsaturation. 5, 6-Celluloseen prepared from cellulose nitrate of high D.S. (degree of substitution) has been shown to be free from nitrate groups.<sup>3</sup> Cellulose nitrate of high D.S. is, however, difficult to prepare and is highly combustible and explosive in nature. The preparation of 5, 6-celluloseen involves replacement of nitrate groups at C<sub>6</sub> by iodine and subsequent dehydroiodination along with hydrogen at C<sub>5</sub>. Hence, if sufficient nitrate groups are present in C<sub>6</sub> position cellulose nitrate of low D.S. may equally serve as a good starting material for preparation of 5, 6-celluloseen. Murray and Purves<sup>4</sup> have shown that in cellulose nitrate of low D.S. at least one-half

of the nitrate groups are at C<sub>6</sub>. As the amount of accompanying oxidation probably depends upon the degree of nitration, preparation of 5, 6-celluloseen from cellulose nitrate of low D.S. may result in a product with lesser degradation.<sup>4</sup> Hence, in the present work cellulose nitrate of D.S.  $\approx 1$  was used as a starting material and conditions have been standardised for introduction of high degree of unsaturation. The composition of the celluloseen product obtained has been established by chromatographic and infra-red methods, and compared with celluloseen obtained from cellulose nitrate of high D.S.

Cellulose nitrate of D.S.  $\approx 1$  was prepared by using a nitrating mixture (H<sub>2</sub>SO<sub>4</sub> + HNO<sub>3</sub> + H<sub>2</sub>O), the composition of which was selected after various trial experiments. Cellulose nitrate was then subjected to iodination in acetone solvent as suggested previously.<sup>3</sup> The dehydroiodination of the resulting 6-iodo-deoxy cellulose nitrate was carried out with alcoholic potassium hydroxide solution for various reaction periods at room temperature and also at 65° C. The maximum unsaturation introduced at both temperatures was of similar order suggesting that increase in temperature had only an effect of accelerating the rate of dehydroiodination. Analysis of typical products at different stages are summarised in Table I.

TABLE I

Original cellulose nitrate		6-Iododeoxy-cellulose nitrate				5, 6-Celluloseen				
Nitrogen (%)	D.S. (ONO <sub>2</sub> )	Iodine (%)	D.S. (iodine)	Nitrogen (%)	D.S. (ONO <sub>2</sub> )	Bromine No.	D.S. (double bond)	Iodine (%)	Nitrogen (%)	% Iodine replaced by double bond
7.16	1.07	30.0	0.52	1	0.16	31	0.31	$\approx 0$	$\approx 0$	58
12.50	2.25	37.7	0.71	1	0.17	39	0.37	$\approx 0$	$\approx 0$	50

The unsaturation introduced in both celluloseen products starting from cellulose nitrate of low as well as high D.S. is of comparable order. The percentage of iodine replaced by

cellulose nitrate of low D.S. as well as its reactivity, it was subjected to acetylation under different conditions. Analysis of the products are summarised in Table II.

TABLE II

Sample	Acetylating agents	Bromine No.	D.S. (double bond)	Acetyl No.	D.S. (acetyl)
5, 6-Celluloseen	..	31	0.31	0	0
"	.. (1) Acetic acid	4	0.04	8.5	0.25
"	.. (2) Peracetic acid	0	0	15.0	0.47
"	.. (3) Standard acetylation	4	0.04	32.0	1.20
"	.. (4) Acetic anhydride	3	0.03	46.0	1.90
"	.. (5) Peracetic acid + standard acetylation	0	0	55.5	2.40
Standard cellulose	.. (1) Acetic acid	0	0	0	0
"	.. (3) Standard acetylation	0	0	62.0	2.90
"	.. (5) Peracetic acid + standard acetylation	0	0	62.0	2.90

double bond is higher in celluloseen product starting with cellulose nitrate of low D.S. Residual nitrate groups in iododeoxy-cellulose nitrate are found to be removed simultaneously. The formation of double bonds is not quantitative in both the cases suggesting the presence of side reactions.

Chromatographic and infra-red studies of 5,6-celluloseen prepared from cellulose nitrate of low D.S. showed it to be a mixed polysaccharide containing elementary units of 5,6-glucoseen, 3,6-anhydro-D-glucose and D-glucose as in the preparation from high D.S. cellulose nitrate. As the percentage of iodine converted into double bond is more in the former, the side reaction, *viz.*, formation of anhydro ring between C<sub>6</sub> and C<sub>3</sub> would be of a lesser order. Preparation of cellulose nitrate of low D.S. is moreover quite simple as compared to that of cellulose nitrate of high D.S. and the product is safer to handle and store. Retention of fibrous structure during iodination of cellulose nitrate of low D.S. considerably simplifies the isolation of all the intermediate products. 5,6-Celluloseen prepared from cellulose nitrate of low D.S. had a higher D.P. as compared to product from cellulose nitrate of high D.S. as observed from copper number values.

In order to get further information about the structure of 5,6-celluloseen prepared from

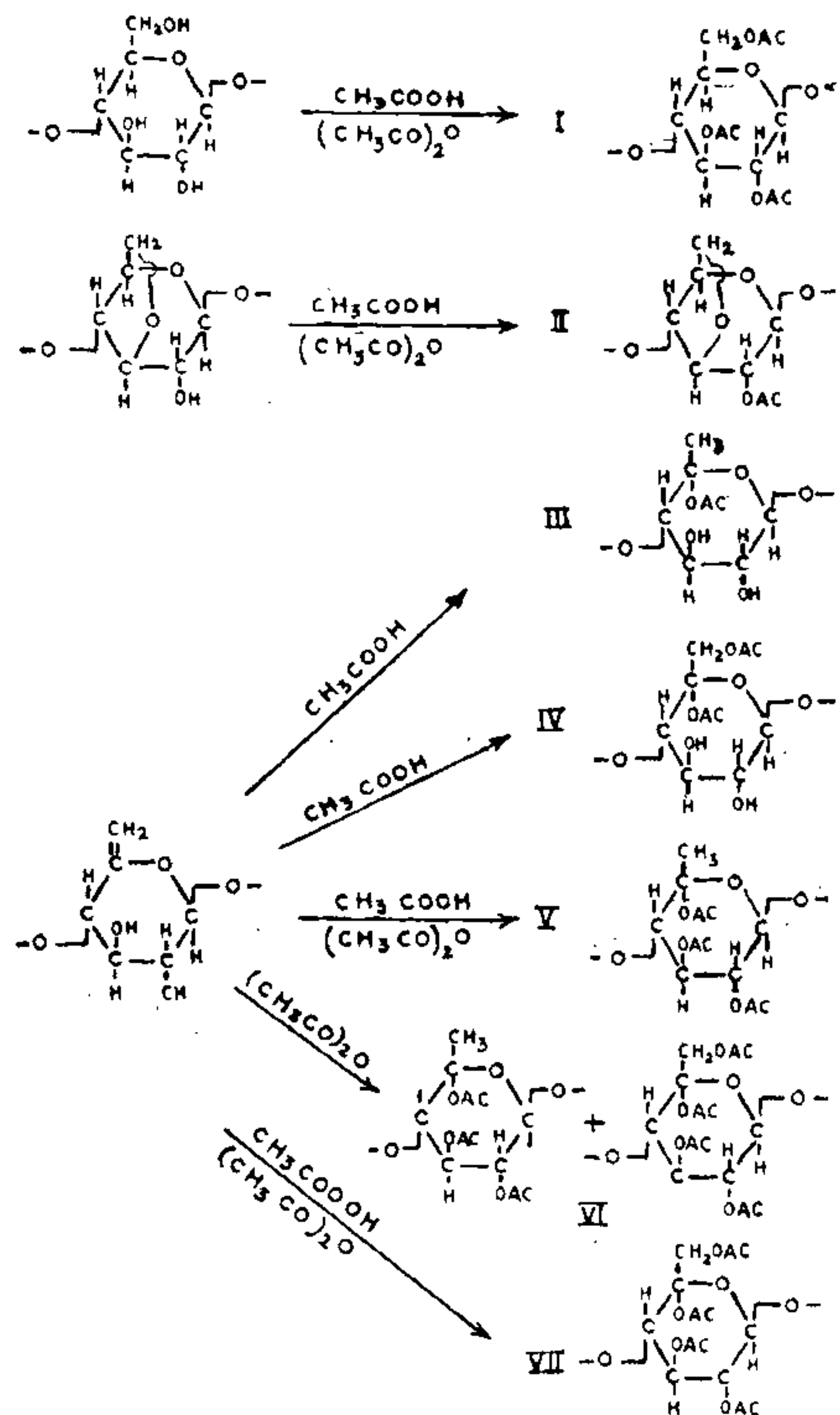
In order to understand the total effect, the reactions of different acetylating agents with the three elementary units in 5,6-celluloseen product have to be considered. D-glucose as well as 3,6-anhydro-D-glucose units are not likely to undergo any reaction with acetic acid and peracetic acid as can be seen from the values for standard cellulose. These two components can react with acetic acid and acetic anhydride mixture in presence of catalyst, forming 2,3,6-triacetyl glucose and 2-acetyl, 3,6-anhydro-D-glucose units respectively as shown by reactions I and II. Hence, difference in values of acetyl number in celluloseen must be attributed to the reaction of 5,6-glucoseen unit only. 5,6-glucoseen can add on acetic acid leading to the formation of 6-deoxy-5-acetyl glucose (III). Peracetic acid is known to introduce hydroxyl groups into olefins.<sup>5,6</sup> During the reaction of peracetic acid with celluloseen, glycol formation may take place at the double bond which would get acetylated forming 5,6-diacetyl glucose (IV). Under standard acetylation conditions involving pre-treatment with acetic acid followed by reaction with acetic anhydride, acetic acid may be initially adding to the double bond as shown by reaction III and other hydroxyl groups get subsequently acetylated giving 6-deoxy 2,3,5-triacetyl glucose units (V). When acetic anhydride alone is used, the reaction is likely to be complex. Acetic acid is bound to be



formed as a result of acetylation and can itself take part in the reaction. A higher value for acetyl number with acetic anhydride alone as

compared to standard acetylation, indicates the possibility of oxidation of double bond of 5,6-glucoseen unit by perchloric acid used as a catalyst leading to formation of epoxy type ring and its subsequent opening up and acetylation of hydroxyl groups produced giving a complex product containing 6-deoxy, 2,3,5-triacetyl glucose and 2,3,5,6-tetracetyl glucose (VI). The highest value is obtained on treatment with peracetic acid followed by standard acetylation procedure leading to the formation of 2,3,5,6-tetracetyl glucose units (VII).

Although it is obvious that some of the above reactions may not be taking place quantitatively and reaction products may be unstable, the reactions proposed above can explain satisfactorily the observed acetyl number values under different acetylation conditions. The above results also show that the standard acetylation procedure for estimation of hydroxyl groups in cellulose derivatives is not applicable when unsaturation exists in the elementary glucose unit of cellulose macromolecules.



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