CHAPTER V

SYNTHESIS OF UNSATURATED DERIVATIVES OF CELLULOSE
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The chemical reactivity of cellulose is limited due to the availability of only one type of functional groups i.e. hydroxyls. With this limited reactivity, many of the derivatives described in the first chapter have been synthesized. As indicated earlier this reactivity of cellulose can be enhanced by physical means such as swelling to make the reaction sites more easily accessible to the reagent. Some complex derivatives can be synthesized by using simple cellulose derivatives as intermediates. The reactivity of these intermediates will depend on the atoms or groups present in them, and here also the limitations will be observed, usually further reactions would be by substitutions.

A new class of derivatives can be obtained by introducing unsaturation into the cellulose molecule itself. Compounds having unsaturation are chemically more reactive than similar saturated compounds. The organic molecules having a triple bond are much more reactive than those having double bonds. In case of unsaturation, a conjugated system again is highly reactive. The literature on unsaturated derivatives of cellulose is very sparse and only few reports are available. Cellulose derivatives having double bonds in a side-chain have been reported. This can
be obtained from unsaturated acids such as acrylic acid and methacrylic acid. Reactions of cellulose with a mixture of unsaturated fatty acids like oleic, linoleic and linolenic acids have been described. Halogenation, thiocyanation and mercuration of the double bonds results in new class of derivatives having biological activity. Cellulose acetates having a pendant double bond have been reported by Faraone and his co-workers. In one recent study by Lifland and Temin, cotton fabrics were converted to derivatives possessing polymerizable pendant double bond.

The introduction of unsaturation into the glucopyranose units of cellulose is another way of modifying cellulose. The changes expected in properties of such cellulose will be more far reaching as the basic structure of cellulose being altered. The glucopyranose unit with three hydroxyl groups offers interesting possibilities for creation of endocyclic and exocyclic double bonds. Many of the methods of carbohydrate chemistry can be employed for the introduction of unsaturation into the cellulose molecule. These derivatives should be regarded as mixed polysaccharides. Rogovin and co-workers have synthesized unsaturated derivatives having a conjugated double bond system in the glucopyranose unit. This was achieved by thermal degradation of cellulose methylxanthate or cellulose dixanthogenide.
The introduction of an exocyclic double bond into the cellulose molecule seems to be easier than the endocyclic bond. For such modifications, the advantage of higher reactivity of primary hydroxyl group is available. Also, such modifications do not alter much the configuration of the molecule.

Usually unsaturation is effected by the procedure of dehydrohalogenation, and it has been reported\textsuperscript{7,8} that iodo-tosyl cellulose when reacted with piperidine leads to unsaturated products. However, this method was not found satisfactory as the cellulose derivative contained some bound piperidine.

Rogovin and co-workers\textsuperscript{9} have synthesized 5,6-celluloseen/6-deoxycellul-5-enose\textsuperscript{7} by treating iodotosyl and iodonitrite derivatives of cellulose with 3% solution of potassium hydroxide in absolute methanol for 24 hours at 20 ± 2°. Similar work has been reported by Achwal and his co-workers.\textsuperscript{25} (The iodo derivatives were prepared by replacement of the ester groups,) They found that although almost complete dehydroiodination of the cellulose derivative had taken place, the number of double bonds produced was about 50% of the theoretical value. This discrepancy in the observed results was ascribed to the side reactions leading to the formation of anhydrides. The 3,6-anhydro derivative is formed by the nucleophilic attack of the OH group at C-3 with elimination of the good leaving group at
C-6. This side reaction was prevented when benzyl and phenylearbamoyl groups were used for blocking the secondary hydroxyls\textsuperscript{10}. Both these groups can be easily removed with retention of the unsaturation. In this work, iodo derivatives and 1.0% methanolic potassium hydroxide for 48 hr at 35° were required. One report\textsuperscript{11} deals with xanthate derivative where the cellulose xanthate is reacted with reagents to give an addition product and the addition product yields olefin on refluxing in acidic water.

The above literature indicates that not much work has been done in this field and it was felt that more basic data and understanding were required for a feasible approach towards the application to cotton and cotton textiles. Therefore, it was considered of interest to investigate the reaction further with the following objectives:

(i) To reduce the number of steps involved in the synthesis of unsaturated cellulose;
(ii) To minimize the side reactions; and
(iii) To reduce the time of reaction (since prolonged time of reaction might affect the structural properties).

This can be achieved by employing halogen or ester derivatives of cellulose, directly prepared by one step reaction and reacting them with very powerful bases to enable elimination reaction quickly and if possible, without side reactions.
Elimination Reactions

An alcohol can be converted to olefin by the process of dehydration or elimination reactions. In the first process water molecule is eliminated in presence of acid and heat. These conditions are dangerous for cellulose structure. The second method of elimination reaction is well-known and for this purpose the alcoholic groups should be replaced with halogen. The reaction of dehydrohalogenation is effected by using a strong base when elimination of hydrogen halide takes place. e.g.,

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{KOH/MeOH}} \text{CH}_3\text{CH} = \text{CH}_2 \]

There are two mechanisms for explaining this reaction; and they bear the same relationship to each other as do the \( S_N1 \) and \( S_N2 \) mechanisms of substitutions. The \( E_1 \) mechanism is elimination, unimolecular which involves one molecule in the rate determining step. The \( E_2 \) mechanism is elimination, bimolecular and involves two molecules in the rate determining steps. It can be illustrated as below:

\[ \xrightarrow{X} \]

\[ \xrightarrow{\text{CH}} \]

\[ \xrightarrow{\text{H}; \text{B}} \]
The base pulls away a proton from carbon, simultaneously a halide ion separates and the double bond forms. Stepwise it can be described as follows:

(i) There is a formation of the bond between the hydrogen and the very strong base, methoxide ion;
(ii) Formation of a $\pi$ bond; and
(iii) Removal of halide ion.

This third step is very important. The halide ion is solvated by the polar solvent (alcohol) and the liberated ion is surrounded by a cluster of these polar molecules. Each solvent molecule is oriented in such a way that the positive end of its dipole is near the negative ion. In short, it is concerted mechanism. Thus, no sooner a hydrogen ion from the $\beta$ carbon is pulled out of the molecule by a base, a halide ion is pulled out by the solvent molecules. This also requires a particular steric arrangement.

In the transition state, the four atoms must be coplanar and trans. In open chain structures, there is usually difficulty in obtaining such an arrangement. In the case of cyclic systems, hydrogens which are cis to the leaving group cannot undergo the $E_2$ reaction and in such cases isomeric products result.
E₂ elimination is similar to $S_N^2$ and requires the presence of base for the slow step. Unlike $S_N^2$, it is a preferred reaction with tertiary halides and is much less successful with primary. Therefore, the requirements for E₂ elimination reactions are: (i) a suitable substrate, (ii) a strong base, and (iii) a polar solvent.

All these three components have significant effect on the rate of reaction and therefore, for effective reaction on cellulose, proper system should be selected.

Substrate: For introduction of unsaturation into cellulose molecule the elimination reaction can be conveniently carried out by taking its halogen derivatives. Methods for the preparation of halogen derivatives are known and some are described in earlier chapters. Among the halogens the order of reactivity as leaving groups is $I > Br > Cl > F$.

Also, the anions of strong acids are found to be good leaving groups. Therefore, the tosylates ($\text{p-me-C}_6\text{H}_4\text{SO}_3^-$, the conjugate base of a very strong acid) yield alkenes very rapidly. In the large anions the mutual polarisability between the anion and the solvent molecule is very high and thus helps in solvation.

Solvent Effects: The behaviour of leaving groups in E₂ reactions varies from solvent to solvent. The selection of solvent is very important because it acts in two ways:
(i) solvation of the anion, and (ii) abstraction of proton. The second purpose is served by the base but some solvents help the base and hence enhance the reactivity. For this purpose solvents are classified as protic solvents and dipolar-aprotic solvents. Protic solvents are those whose hydrogen is attached to oxygen or nitrogen and are appreciably acidic, and through hydrogen bonding they solvate the anions. Sometimes the reactivity is lowered here, because they also form H-bonds with the base. Water, methanol etc. fall in this group.

The other class of polar solvents having moderately high dielectric constants and which do not contain acidic hydrogen are known as dipolar-aprotic solvents. When ionic compounds are dissolved in these solvents, the cations are solvated most strongly and anions are left relatively untouched and highly reactive. Bases are tremendously more basic and nucleophiles are highly nucleophilic in these solvents. N,N-Dimethyl formamide (DMF), dimethylsulfoxide (DMSO), acetone, hexamethylphosphoramide (HMPA) etc. are examples of this class and are usually recommended because they are cheap and water miscible. In dipolar aprotic solvents anions are solvated by ion-dipole interactions, on which is super-imposed an interaction due to the mutual polarisability of the anion and the solvent molecule, which is greatest for large anions.
Base: While selecting the base, not only the basicity, but also the effect leading to the type of reaction (elimination or substitution) should be considered. The use of inorganic bases like NaOH, KOH along with methanol have been reported for elimination reactions.

A much stronger base is generated when alcohol is reacted with active metals like Na, K, Mg and Al. Alkoxides are more basic than OH$^-$ of the above system. Even among the alkoxides, the structure of alcohol contributes much to the basicity. Presence of alkyl groups due to their inductive effect render the alcohol less acidic than water. The greater the number of alkyl groups, lesser will be the acidity of the alcohol and stability of the ionized species.

\[
\begin{align*}
R & \\
\downarrow & \\
R & \rightarrow \text{C} \rightarrow O - H & \rightarrow & \text{C} \rightarrow O^- + H^+ \\
\uparrow & \\
R & 
\end{align*}
\]

Alkoxides derived from such alcohols are strongly basic and they favour E$_2$ elimination over S$_{N2}$ substitution. Because of crowding of the groups in alkoxide molecule, the nucleophile cannot get close enough to the backside of the leaving group to start a new bond formation. Thus, the base \((\text{CH}_3)\_3\text{C} - O^-\) is more effective than \(\text{CH}_3\_\text{CH}_2 - O^-\) or \(\text{OH}^-\) for elimination reactions.
Potassium t-Butoxide (t-BuOK)/Dimethyl Sulfoxide (DMSO) System and Silver Nitrate (AgNO₃)/DMSO System

$t$-BuOK is one of the most powerful bases known. Its chemistry and uses have been reviewed recently\textsuperscript{12}. The observation by Cram\textsuperscript{13} that DMSO greatly enhances the basic strength of $t$-BuOK led to extensive use of this system. For a creation which requires a strong proton abstractor, e.g., elimination, $t$-BuOK in DMSO has many attractive features. In this mixture $t$-BuO$^-$ and dimesyl anions\textsuperscript{14} exists and the basicity is governed by the purity of $t$-BuO$^-$ and exclusion of water from DMSO. With this system the reaction occurs under much milder conditions and many times faster than other systems\textsuperscript{15}. In the present investigations also this system has been employed.

The AgNO₃/DMSO system, like AgF/Pyridine gives good results with iodo derivatives. Ag ion has very strong affinity for halogens while DMSO has powerful cationic solvation property. These two properties can be combined to give a good reagent for our purpose. It also offers a simple alternative to the other commonly used organic bases which are used in routine synthetic work. The solubility of AgNO₃ in DMSO at 25°C is 130 g/100 ml. This reagent has been reported by Mehta\textsuperscript{16} who has used it for dehydrohalogenation of terpenes. It has also been successfully employed in this laboratory\textsuperscript{17} on model carbohydrate compounds.
Reactions of Double Bonds

Addition Reactions

In the normal course of reaction the addition reaction across the double bond follows the Markovnikov's rule, which is by ionic mechanism. In the presence of free radical generators e.g., peroxides, the anti-Markovnikov addition takes place. In the reactions with unsaturated cellulose derivatives the addition is brought about by the second method. Rogdvin² has studied the reaction of simple compounds such as chloroform, carbon tetrachloride, methyl-monochloroacetate, phosphorus trichloride, etc. with unsaturated cellulose.

\[
\begin{align*}
\text{CH}_2 & \quad + \quad R_1R_2 \quad \xrightarrow{\text{hv}} \quad \text{CH}_2R_2 \\
\text{OH} & \quad \text{OH} \\
\end{align*}
\]

The initiators like benzoylperoxide, tributylperoxide, UV light etc. were employed. In our studies we have attempted the addition of chloroform across the double bond using UV light and benzoylperoxide as initiators.

Grafting

Grafting of styrene monomer on the pendant double bonds of cellulose acetocrotonate and cellulose acetomaleate, as
well as cellulose acetate modified with methacryloyl-ethyleneimine has been achieved by Faraone et al.\textsuperscript{3} using benzoyl peroxide as initiator. Recently, Temin and Lifland\textsuperscript{4} have reported grafting at the pendant double bonds. In their studies they have converted the cotton fabrics to acrylamidomethyl cotton, allyl cotton and cotton maleate. These modified cottons were copolymerized with various monomers to produce cross-linked fabrics employing ceric ions as initiator. No report is available dealing with grafting onto the exocyclic double bond of glucopyranose unit of cellulose.

In our studies we have attempted grafting of acrylonitrile at the double bond using ceric ion system as initiators.
RESULTS AND DISCUSSION

The reaction of dehydrohalogenation has been studied on chloro and iodo derivatives of cellulose. For the reactions in homogeneous phase, the chlorodeoxyxcellulose acetate derivatives were used.

Reactions of Chlorodeoxyxcellulose, Chlorodeoxyxcellulose Acetate and Iodotosylxcellulose with Bases

Efficiency of KOH/MeOH and t-BuOK/DMSO as reagents for dehydrohalogenation were studied on chlorodeoxyxcelluloses. The conditions for dehydrohalogenation, as reported by Rogovin and co-workers, were employed for reactions with KOH/MeOH. With this system, the conversion to unsaturated derivative was not quantitative as can be seen from Table I. Thus when chlorodeoxyxcellulose and its acetate are reacted with KOH/MeOH at 72°C for 24 hr, only 40 to 50% conversion is obtained. The conversion is calculated from the difference of double bonds expected (based on initial D.S. of chlorine) and total number of double bonds obtained. The residual chlorine after reaction should also be considered. Thus, chlorodeoxyxcellulose of D.S.(Cl) 0.15, is theoretically expected to give 15 double bonds ΣD.S.(C=C), 15 and Cl% 0.07. However, the reaction product has a D.S.(Cl) of 0.036 and therefore, the theoretically expected value of double bonds is 0.114 D.S. whereas actual value is 0.046 giving a percentage conversion of 40.3%. In the case of
the acetate derivative, under similar conditions, 52.3\% conversion is observed, the product having a residual D.S. (Cl) 0.04. These results clearly indicate that some side reactions such as dehalogenation or 3,6-anhydro ring formation are taking place. Bogovin et al\(^9\) have reported the formation of 3,6-anhydro ring as a parallel reaction. In the case of the acetate derivative, deacetylation also takes place when this reagent is used.

With the \(\text{t-BuOK}/\text{DMSO}\) system, the conversion is almost quantitative. Thus, chlorodeoxy cellulose with D.S.(Cl) 0.24, expected D.S.(C=C) 0.24 when reacted with \(\text{t-BuOK}/\text{DMSO}\) at 28\(^\circ\) for 20 hr, gives a product having 18 double bonds with D.S.(C=C) 0.178 per 100 glucopyranose units; with a residual D.S.(Cl) 0.051. This amounts to the total conversion of 94.2 percent. The acetate derivatives give 100 percent conversion, when reacted with this system at 95\(^\circ\) and 28\(^\circ\) for 4 hr and 1 hr respectively. These data indicate that although chlorine is not completely removed but whatever is eliminated results in the formation of double bonds. There are no side reactions such as dehalogenation or 3,6-anhydro ring formation and only under drastic conditions deacetylation is observed. The conditions used in experiment 2(c) are milder and of short duration than that employed in 2(b). It is evident from these two experiments that increase in reaction time or temperature is not very
effective for this reaction, but a higher concentration of the reagent can push the reaction to the right leading to complete dehydrohalogenation of the product.

With the iodotosylcellulose, t-BuOK/DMSO gave a conversion of 56.5% and 66.6% only. Increase in concentration of the t-BuOK leads to higher unsaturation however, the D.S. (tosyl) at secondary hydroxyls has reduced, which indicates that detosylation has taken place. The possibility of formation of 3,6-anhydro ring cannot be excluded, since some of the hydroxyls at C-3 are not blocked and some are made free by the departure of the tosyl groups due to hydrolysis.

Many conclusions can be drawn from the results reported in Table I. The ester (acetyl, tosyl) groups are hydrolyzed but under mild conditions only tosyl groups are hydrolyzed. Also the reaction of dechlorination is not observed but replacement of iodine by hydroxyl is noticed, which is true since chloro groups are more stable than iodo groups. Chlorine is more electronegative than iodine, and since iodine is a better leaving group it can go more easily than Cl⁻ by solvation effect. Thus, when the hydrogen at C-3 is ionized, the C-I bond can break by solvation of the anion iodine, and 3,6-anhydro derivative will result. In the case of chlorine, the probability of this type of reaction is less, because DMSO will solvate chlorine less than iodine. Chlorine can go if C-6 becomes rich in electrons and acquires a more
### TABLE I
PREPARATION OF 5,6-CELLULOSEEN

<table>
<thead>
<tr>
<th>No.</th>
<th>Initial Product</th>
<th>Dehydrohalogenation Conditions</th>
<th>5,6-Celluloseen Conversion*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Reagent</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>1.</td>
<td>Chlorodeoxycellulose</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(a) D.S. (Cl), 0.15</td>
<td>KOH/MeOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b) D.S. (Cl), 0.24</td>
<td>t-BuOK/DMSO</td>
</tr>
<tr>
<td>2.</td>
<td>Chlorodeoxycellulose Acetate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(a) 1.35 0.25</td>
<td>KOH/MeOH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b) 1.35 0.25</td>
<td>t-BuOK/DMSO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(c) 1.88 0.58</td>
<td>t-BuOK/DMSO</td>
</tr>
<tr>
<td>3.</td>
<td>Iodotosylcellulose</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(a) D.S.(Iodine), 0.69 1 mole</td>
<td>25 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b) D.S.(Tosyl), 0.41 4 mole</td>
<td>25 2</td>
</tr>
</tbody>
</table>

* Denotes conversion into the unsaturated product only.
Fig. 1: IR Spectra of Unsaturated Cellulose Prepared from Chlorodeoxy Cellulose
negative charge. This is only possible when proton at C-5 is abstracted, and that electron pair will be retained by C-5 which will be transferred to C-6 because of the presence of chlorine. Thus chlorine, under combined effects of solvation as well as repulsion, will leave the position. The reactions of model compounds with AgNO₃/DMSO in this laboratory has confirmed this. Chloro derivatives did not react even under drastic conditions but iodo compounds gave readily the unsaturated products. When this reagent system was used with iodo cellulose derivative good results were obtained. The infrared spectra of these unsaturated products are given in Figure 1. Strong absorption bands are observed at 2900 to 2950 cm⁻¹ region and 1658 to 1638 cm⁻¹ region, characteristic of stretchings due to >CH₂ and to that of a terminal exocyclic carbon-carbon double bond respectively. There is no absorption in the region of 800 to 900 cm⁻¹, indicating absence of 3,6-anhydro ring. In spectra numbers I and II of Figure 2, there are strong absorption bands at 1750 cm⁻¹ indicating presence of ketonic groups of the acetyl ester.

**Reaction of Iodotosylcellulose with AgNO₃/DMSO**

The AgNO₃/DMSO system has been studied on model carbohydrate compounds in this laboratory, and it was found that it works efficiently only with the iodo derivative. With chloro and bromo derivatives no reaction was found to take place and under drastic conditions (sealed tube at 100° for 8 hr) replacement of halogen atoms by nitrate group was observed.
Fig. 2: IR Spectra of Unsaturated Cellulose Prepared from Chlorocellulose Acetate

(1) Room Temperature (30°C), 2 hr; (II) 95°C, 4 hr.
With iodosylcellulose the reaction proceeds smoothly (100° for 1.5 hr), and silver iodide precipitates out. After removal from the mixture and many washes with distilled water, the product was analyzed. There was found considerable variation in the values of iodine content. This indicated that some adsorbed or trapped iodine in the form of AgI was still present in the fibrous reaction product and which was not removable by cold or hot water. The product decolourized bromine in CCλ₄ and dilute KMnO₄ solutions indicating the unsaturated nature of the product.

Reactions of Tosylcellulose and Its Acetate

For the homogeneous reaction system tosylcellulose acetate was employed and the reaction with t-BuOK/DMSO was studied at 95° and 28° (Table II). The analysis of the
IR Spectra of
(I) Unsaturated Cellulose from Mesityl Cellulose
(II) Mesityl Cellulose

Fig. 3
TABLE II

REACTION OF TOSYLCELLULOSE ACETATE* WITH t-BuOK/DMSO

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Reaction Temperature (°C)</th>
<th>Reaction Time (hr)</th>
<th>Composition of 5,6-Celluloseen %</th>
<th>Conversion %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>D.S. (Acetyl) D.S. (Tosyl) Br. No. D.S. (C = C)</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>95</td>
<td>3</td>
<td>1.38 0.12 12.8 0.16</td>
<td>76.1</td>
</tr>
<tr>
<td>2.</td>
<td>RT</td>
<td>5</td>
<td>1.87 0.27 9.0 0.15</td>
<td>71.4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td></td>
<td>1.67 0.16 11.0 0.16</td>
<td>76.1</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td></td>
<td>1.4 0.14 13.5 0.18</td>
<td>85.7</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td></td>
<td>1.4 0.13 14.3 0.21</td>
<td>100.0</td>
</tr>
</tbody>
</table>

* D.S. Tosyl (Total) = 0.56; D.S. Tosyl C-6 = 0.21

starting material (D.S. tosyl 0.56) revealed that tosyl groups were located both at primary and secondary hydroxyl groups of the glucopyranose units. The estimation of tosyl groups at C-6 (primary hydroxyl) was carried out by the Oldham-Rutherford \(^\text{18}\) method of iodination which was used by Cramer and Purves \(^\text{19}\) for a similar purpose. In this method, after iodination with NaI in acetone, the D.S. of iodine represents the D.S. of tosyl at the primary position, since such a replacement of tosyl group takes place almost selectively and quantitatively at such positions only. In the reaction at 95° for 3 hr, 16 double bonds are obtained whereas at room temperature almost the same conversion is achieved in 5 to 10 hr. It is quite possible, that at 95°, complete reaction had taken place in less than 3 hr; therefore further treatment has not
brought any significant change except that some side reactions such as deacetylation and detosylation might have taken place. These side reactions are faster at higher temperature. The D.S. (tosyl) at C-6 is 0.21 and after 30 hr treatment at 28\(^\circ\), about 21 double bonds are achieved. This is complete conversion, however the main part of it has taken place in the initial 5 hr. Since the secondary groups are blocked with acetyl and some are blocked less with tosyl, there is a possibility of formation of 3,6-anhydro ring, which is also evident from the 100% conversion to the olefin. In absence of such blocking groups such a prolonged treatment would have definitely led to the side reaction of 3,6-anhydro formation. The main reaction is again accompanied by detosylation and deacetylation. Increase in concentration of the t-BuOK, might give these results in a shorter reaction time. Unlike KOH/MeOH treatment, all the acetyl and tosyl groups are not knocked off, which also suggests that the t-BuOK/DMSO favours elimination over S\(_{N2}\) substitution. The Infrared spectra are given in Figure 4, where absorption bands due to >C = O group of acetyl, and an exocyclic double bond are observed.

The effect of concentration of t-BuOK, temperature and reaction time was studied employing tosyl cellulose (D.S. tosyl, 1.1; D.S. at C-6 0.69). The results on the reactions of tosylcellulose with different molar proportions of t-BuOK,
Fig. 4: IR Spectra of Unsaturated Cellulose from Tosyl Cellulose Acetate.
(I) 95°C, 3 hr; (II) Room Temperature (30°C), 5 hr.
are given in Table III(a). It is observed that with increase in concentration of the reagent, the D.S. (C=C) also increases. The detosylation is a parallel reaction and about 80 percent conversion is achieved, when 4 moles of the reagents are used. The results also indicate that the elimination takes place via E₂ mechanism. In all the experiments, the possibilities of 3,6-anhydro formation cannot be excluded, since secondary positions are not blocked. With 6-mole proportions of the reagent, there is no further increase in unsaturation. This indicates that the reaction of 3,6-anhydro formation is taking place simultaneously. The reaction period of 23 hr is not required. This can be seen from Table III(b), where the reaction is carried out (using 1:1 molar proportion of substrate and the reagent) for 2, 7 and 30 hr. No change in the values of D.S. (C=C), is observed and only detosylation proceeds with reaction time. The increase in reaction temperature (65°) does not give more of unsaturation and only a D.S. (C=C) of 0.21 is obtained in 2 hr compared to 0.33 at room temperature. Also, at higher temperature the predominance of detosylation reaction is observed and from the values of D.S. (tosyl) and D.S. (C=C), it can be stated that 3,6-anhydro formation might have taken place during the reaction. Thus, for better conversion, about 4 moles of the reagent can be suggested. (Fig. 5-7)

The studies by Snyder and Soto on the reaction of t-BuOK in DMSO with sulfonate esters of primary and secondary
Fig. 5: IR Spectra of Unsaturated Cellulose Prepared from Tosyl Cellulose (1 mol, 30°C, 23 hr)
Fig. 6: IR Spectra of Unsaturated Cellulose Prepared from Tosyl Cellulose (4 mol, 30°C, 23 hr)
### TABLE III(a)

**REACTION OF TOSYL CELLULOSE* WITH DIFFERENT MOLES OF t-BuOK IN DMSO**

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Reaction Temp. (°C)</th>
<th>Reaction Time (hr)</th>
<th>Molar Proportion of t-BuOK</th>
<th>Composition of 5,6-Cellulose</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D.S. (Tosyl)</td>
<td>Br. D.S. (C = C)</td>
</tr>
<tr>
<td>1.</td>
<td>RT 23</td>
<td>1</td>
<td>0.27</td>
<td>26.7</td>
<td>0.31</td>
</tr>
<tr>
<td>2.</td>
<td>28</td>
<td>2</td>
<td>0.05</td>
<td>41.7</td>
<td>0.38</td>
</tr>
<tr>
<td>3.</td>
<td></td>
<td>3</td>
<td>0.02</td>
<td>45.7</td>
<td>0.42</td>
</tr>
<tr>
<td>4.</td>
<td></td>
<td>4</td>
<td>0.05</td>
<td>61.5</td>
<td>0.58</td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td>6</td>
<td>0.02</td>
<td>62.1</td>
<td>0.58</td>
</tr>
</tbody>
</table>

*D.S. Tosyl (Total): 1.1; D.S. Tosyl (C-6): 0.69

### TABLE III(b)

**REACTION OF TOSYL CELLULOSE* WITH t-BuOK/DMSO**

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Reaction Temp. (°C)</th>
<th>Reaction Time (hr)</th>
<th>Composition of 5,6-Cellulose</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>D.S. (Tosyl)</td>
<td>Br. D.S. (C = C)</td>
</tr>
<tr>
<td>1.</td>
<td>RT 2</td>
<td>0.37</td>
<td>26.3</td>
<td>0.33</td>
</tr>
<tr>
<td>2.</td>
<td></td>
<td>0.29</td>
<td>30.2</td>
<td>0.35</td>
</tr>
<tr>
<td>3.</td>
<td></td>
<td>0.25</td>
<td>30.3</td>
<td>0.35</td>
</tr>
<tr>
<td>4.</td>
<td>65</td>
<td>0.26</td>
<td>28.0</td>
<td>0.16</td>
</tr>
<tr>
<td>5.</td>
<td>0.5</td>
<td>0.19</td>
<td>20.3</td>
<td>0.21</td>
</tr>
<tr>
<td>6.</td>
<td>1.0</td>
<td>0.18</td>
<td>20.8</td>
<td>0.22</td>
</tr>
<tr>
<td>7.</td>
<td>1.5</td>
<td>0.18</td>
<td>22.3</td>
<td>0.23</td>
</tr>
<tr>
<td>8.</td>
<td>22.0</td>
<td>0.19</td>
<td>20.0</td>
<td>0.21</td>
</tr>
</tbody>
</table>

*D.S. Tosyl (Total): 1.1
D.S. Tosyl (C-6): 0.69
Fig. 7: IR Spectra of Unsaturated Cellulose Prepared from Tosyl Cellulose (1 mol, 30 hr, 30°C)
aliphatic alcohols and of conformationally flexible alcohols, should be mentioned here. They found that esters of cyclic and secondary acyclic alcohols give alkenes in about 80% yield and only traces of ethers (by substitution) are obtained. The benzene sulfonates of secondary alcohols can be converted to alkenes in yields of 80% whereas in case of primary alcohols the yields are lower because of the competing reaction of ether formation. They have also found that with benzene sulfonates of typical primary and secondary alcohols, the ether-alkene ratio is significantly higher in reactions with sodium methoxide in DMSO than with t-BuOK in DMSO\textsuperscript{21}. In another study\textsuperscript{22} about 83% yield of cyclohexene has been reported after 30 minutes' stirring at 20-25° of solution of cyclohexylbenzene sulfonate and t-BuOK-DMSO.

In our experiments with tosylhalo-, mesyl- and tosyl-celluloses, and cellulose acetate derivatives the products after reaction were found to be powdery, probably due to alkaline degradations. Under the swollen state of the ester derivatives in DMSO, the alkaline treatment in presence of air can cause tremendous damage to the structure. To retain the sliver form of the final product, the reaction was carried out with low tosyl D.S. so that less swelling would take place. The results are given in Table IV. The product had fibrous nature but less number of double bonds.
TABLE IV
REACTION OF TOSYLCELLULOSE* WITH t-BuOK/DMSO

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Reaction</th>
<th>Temperature (°C)</th>
<th>Time (hr)</th>
<th>Molar Composition</th>
<th>% Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Propor-5,6-Celluloseen</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>D.S. of t-BuOK (Tosyl) (C = C)</td>
<td>D.S. of C-6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>t-BuOK (Tosyl) (C = C)</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>25</td>
<td>2</td>
<td>0.1</td>
<td>0.028</td>
<td>0.05</td>
</tr>
<tr>
<td>2.</td>
<td>25</td>
<td>23</td>
<td>4</td>
<td>-</td>
<td>0.08</td>
</tr>
</tbody>
</table>

* Total D.S. (Tosyl) : 0.17
  ** (C-6) : 0.11

The analysis indicated that the conversion percent is the same as observed earlier with high D.S. tosyl cellulose under similar conditions.

Similar reactions were carried out on tosylated fabrics using low D.S. (0.56) and high D.S. of tosyl (Table V). In these cases, the amount of tosyl at C-6 was not ascertained. The reaction takes more time for maximum conversion as compared to the reaction with cotton slivers; this is because of the woven structure of the fabric. As indicated earlier, other side reactions also take place, and quantitative conversion is not possible under these conditions.

The fabrics containing double bonds are brown in colour, brittle and have a horny feel. Though they retain the fabric structure, they do not have any strength which indicates a high degree of degradation.


<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Molar Proportion of t-BuOK</th>
<th>Reaction Temperature (°C)</th>
<th>Time (hr)</th>
<th>Composition of 5,6-Cellulose</th>
<th>D.S. (Tosyl)</th>
<th>Br.</th>
<th>D.S. (C = C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>30 (RT)</td>
<td>2</td>
<td>0.374</td>
<td>3.8</td>
<td>0.048</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>&quot;</td>
<td>20</td>
<td>0.202</td>
<td>4.34</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>&quot;</td>
<td>2</td>
<td>0.026</td>
<td>10.7</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>&quot;</td>
<td>20</td>
<td>0.02</td>
<td>10.6</td>
<td>0.117</td>
<td></td>
</tr>
</tbody>
</table>

*D.S. TOSYL (TOTAL) = 0.53

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Molar Proportion of t-BuOK</th>
<th>Reaction Temperature (°C)</th>
<th>Time (hr)</th>
<th>Composition of 5,6-Cellulose</th>
<th>D.S. (Tosyl)</th>
<th>Br.</th>
<th>D.S. (C = C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>30 (RT)</td>
<td>2</td>
<td>0.632</td>
<td>6.9</td>
<td>0.104</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>&quot;</td>
<td>9</td>
<td>0.376</td>
<td>13.4</td>
<td>0.17</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>&quot;</td>
<td>20</td>
<td>0.214</td>
<td>15.6</td>
<td>0.172</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>&quot;</td>
<td>2</td>
<td>0.14</td>
<td>20.7</td>
<td>0.215</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>&quot;</td>
<td>9</td>
<td>0.033</td>
<td>26.5</td>
<td>0.247</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>&quot;</td>
<td>20</td>
<td>0.023</td>
<td>23.9</td>
<td>0.22</td>
<td></td>
</tr>
</tbody>
</table>

*Bauer et al.* have reported a 80 percent conversion to unsaturated product and absence of the side reaction of 3,6-anhydroformation. They employed benzyl and phenyl-carbamoyl derivatives for blocking the secondary hydroxyls. The cellulose derivatives employed in our studies, like other organic derivatives, react with this system many times faster than KOH/MeOH system. The side reactions are less when higher
concentration of the base is used and the conditions of the reaction are milder. Acetate groups can be used for blocking the secondary hydroxyls since they are not easily removed under some of these conditions. The degradation of the polymeric chain during the reaction may be minimized by conducting the experiment under a nitrogen atmosphere.

The effect of KOH/DMSO system was studied by dissolving KOH in minimum quantity of methanol followed by dilution of the solution with DMSO to make it 9 percent. It was found that tosyl cellulose (D.S. tosyl C-6, 0.69) when reacted with this system gave about 20 double bonds. The KOH/MeOH system reacted with tosyl cellulose and gave 3,6-anhydro glucose residues. The presence of DMSO in the system may be considered responsible for this difference.

Attempts to introduce unsaturation between C-2 and C-3 in the glucopyranose rings of cellulose were made by using 6-O-trityl, 2(3) tosylcellulose. It has been reported that this derivative reacts with KOH/MeOH to give 2,3-anhydro ring. The t-BuOK/DMSO system was tried on this derivative, and it was found that the reaction product decolourised bromine and KMnO₄ solutions. But in the quantitative determination it did not give any value of unsaturation. However, the infrared spectra (Figure 8) showed absorption bands for unsaturation.
Fig. 8: IR Spectra of Reaction Product of 6-O-Trityl, 2(3)-Tosyl Cellulose with t-BuOK in DMSO
Addition Reactions

Addition reactions were carried out on the fabrics containing 8 and 20 double bonds. The results are given in Table VI. As an initiator, benzoyl peroxide gave inferior results than UV light. This observation is in conformity with the results of Rogovin and co-workers. Using UV light as initiator and unsaturated product having 44 double bonds, they were able to react carbontetrachloride with 20 double bonds 9.8% chlorine, D.S.(Cl) 0.2 which indicated 45% addition reaction at the double bond.

TABLE VI
ADDITION REACTION OF CHCl₃

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Initiator</th>
<th>Starting Material</th>
<th>Reaction Time</th>
<th>% Cl Before Reaction</th>
<th>% S Before Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>UV light</td>
<td>Fabric with 8 double bonds</td>
<td>16 hr</td>
<td>1.12</td>
<td>8</td>
</tr>
<tr>
<td>2.</td>
<td>BzO₂ (10%, on wt. of fabric)</td>
<td>&quot; &quot;</td>
<td>2 days</td>
<td>1.28</td>
<td>8</td>
</tr>
<tr>
<td>3.</td>
<td>BzO₂ (10%)</td>
<td>Fabric with 20 double bonds</td>
<td>20 hr</td>
<td>0.42</td>
<td>-</td>
</tr>
<tr>
<td>4.</td>
<td>BzO₂ (20%)</td>
<td>&quot; &quot;</td>
<td>20 hr</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>5.</td>
<td>BzO₂ (10%)</td>
<td>&quot; &quot;</td>
<td>3 days</td>
<td>1.2</td>
<td>-</td>
</tr>
</tbody>
</table>
In our studies, it was observed that when chloroform is reacted with fabric containing 8 double bonds, 1.1 to 1.3% chlorine is obtained using UV light (16 hr) or \( \text{Bz}_2\text{O}_2 \) (10%, 2 days) as initiator. This indicates some addition across the double bond. The residual sulfur remains unaffected. Similar studies on fabrics having 20 double bonds (without residual tosyl groups) revealed that the increase in concentration of benzoyl peroxide (above 10%; 8-10% have been reported to give good conversion) did not have much effect, but increase in reaction time gave better results. However, under the conditions employed, all the double bonds did not undergo addition reaction.

**Grafting Reactions**

Grafting across the double bond was studied using ceric ion initiating system. This system has been successfully employed for direct grafting on cellulose as well as for grafting onto pendant double bonds. For comparison, three substrates, viz., ordinary fabric, tosylated fabric and fabric containing double bonds were employed. The results are shown in Table VII. After grafting, increase in weight is observed in all the three experiments, but on extraction with hot DMF to remove homopolymer loss in weight is observed in case of modified cellu-loses. This is due to the removal of tosyl groups
### TABLE VII

**GRAFTING ON UNSATURATED CELLULOSES**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Dry weight (Drying over P₂O₅)</td>
<td>1.0166</td>
<td>0.9101</td>
<td>0.8856</td>
<td>0.210</td>
</tr>
<tr>
<td>2.</td>
<td>After grafting</td>
<td>1.3583</td>
<td>0.9278</td>
<td>0.9068</td>
<td>0.223</td>
</tr>
<tr>
<td>3.</td>
<td>After extraction with DMF for 24 hr</td>
<td>1.3055</td>
<td>0.4994</td>
<td>0.527</td>
<td>0.211</td>
</tr>
<tr>
<td>4.</td>
<td>Drying over P₂O₅</td>
<td>1.2865</td>
<td>0.4975</td>
<td>0.524</td>
<td>0.209</td>
</tr>
<tr>
<td>5.</td>
<td>Difference in Weight</td>
<td>+0.1699</td>
<td>-0.4126</td>
<td>-0.3616</td>
<td>-0.001</td>
</tr>
<tr>
<td>6.</td>
<td>% Grafting</td>
<td>16.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7.</td>
<td>Nitrogen, %</td>
<td>4.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8.</td>
<td>IR</td>
<td>Positive</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
</tbody>
</table>

After 24 hr extraction with hot DMF. Probably the tosyl groups were hydrolyzed during the reaction in acidic medium and trapped in the structure which were consequently removed at the time of extraction with DMF. The sulfur is found absent after the solvent extraction treatment.

To avoid this, grafting was carried out on products having 20 double bonds and no residual tosyl groups (Table VII).
No change in weight was observed after DMF extraction, which showed that, grafting did not take place. This inference was supported by absence of nitrogen and by infrared analysis. The IR spectra of ordinary fabric grafted with acrylonitrile shows absorption band at 2280 cm\(^{-1}\) which is absent in case of IR of other substrate (Figure 9).

Lifland et al\(^4\) have reported grafting at pendant double bonds using ceric-ion initiating system whereas Faraone and co-workers\(^2\) have reported grafting of styrene at pendant double bonds using Bz\(_2\)O\(_2\) initiator.

**Hydrolysis**

The unsaturated cellulose derivatives, prepared by t-BuOK/DMSO method, showed high resistance towards acid hydrolysis. Achwal\(^25\) carried out hydrolysis experiments on the unsaturated products prepared by KOH/MeOH method. He observed that with 72% sulfuric acid at 120°C for 24 hr only 50% hydrolysis took place. He was however successful in getting methyl glucosides after methanolysis with methanolic hydrogen chloride.

Our attempts to hydrolyze the unsaturated derivatives were not successful and almost the same weight of material was recovered. Under the usual conditions of hydrolysis almost 95 to 98% of the original was recovered as a dark product. The products having unsaturation but no residual
Fig. 9: IR Spectra (Mull) of Fabrics Grafted with Poly-acrylonitrile
sulfur were also tried and after acid treatment (H₂SO₄), the material was filtered, residue washed with distilled water to remove acid and dried and analyzed for sulfur. It was found that sulfur was present but not as much as it should appear after complete addition across the double bond. The very presence of sulfur suggests that some addition of the elements of sulfuric acid have taken place across the double bond. However, the examination of filtrate (after neutralization and resin treatments) by paper chromatography revealed the presence of α-glucose, 6-deoxy-5-keto-β-D-glucose (Isorhmannose) and 3,6-anhydro-β-D-glucose.

The reasons for high resistance of unsaturated cellulose to acid hydrolysis may be the presence of 3,6-anhydro ring and hornification. In some of the IR spectra of unsaturated cellulososes absorption bands are seen at 810, 840 or 900 cm⁻¹ which are characteristic of 3,6-anhydro ring²²,²⁵. This indicates, that 3,6-anhydro ring has resulted wherever the secondary groups are not protected. Now, looking at the reports on properties of 3,6-anhydro cellulose, Gardner and Purves²⁶ have prepared 3,6-anhydrocellulose by alkaline deacylation of a partly substituted tosyl cellulose acetate. The anhydrocellulose obtained was insoluble in solvents in which ordinary cellulose dissolves. Rogovin²⁷ has reported that the introduction of anhydro rings into the cellulose molecule can change its properties significantly, particularly its stability to the action of hydrolyzing agents.
The work on introduction of unsaturation in cellulose using tosylcellulose and KF in ethylene glycol was carried out in this laboratory. The products were hydrolyzed to the repeating unit level. However, it was observed that the crystallinity increased as the unsaturation increase, and difficulty in hydrolyzing the product of high unsaturation was experienced.

In our experiments, the reagent is entirely different and highly alkaline. It was found that the product after treatment with this reagent has high percentage of crystallinity. The ester derivatives swells in this system, groups are knocked off and the swelling agents are removed. This perhaps leads to "hornification" which arises from the formation of stronger bonds between the mobile cellulose chains of the swollen structure as it collapses in drying. The role of DMSO as a hydrogen bond breaker should also be emphasized, since after removal of DMSO, the bonds might reunite in a more systematic way.

The enzymatic hydrolysis was not successful and no action on the modified celluloses was observed, except that only small amount of glucose could be observed as spots on paper chromatography examinations.
EXPERIMENTAL

Materials

Chlorodeoxycellulose and Chlorodeoxyceellulosediacetate

Chlorodeoxycellulose and its acetate were prepared from activated cotton slivers and cellulose diacetate respectively by the procedure described in Chapter III, using methanesulfonyl (mesyl) chloride in DMF.

Mesylcellulose

Activated cellulose (5 g) after squeezing the benzene was suspended in pyridine, filtered and the material was again suspended in dry pyridine (250 ml) and the suspension cooled to 0°. To this was added with vigorous shaking mesyl chloride (21.2 g), previously cooled to 0°. The reaction was allowed to proceed at room temperature for 48 hr. The cellulose did not dissolve and the colour of the liquid turned to reddish-brown. At the end of this period the reaction product was removed by filtration and washed with hot water until the washings were colourless. The water was displaced with acetone washings, and the product, a light tan solid was air-dried. D.S. (Mesyl), 0.58.

Iodotosyl Cellulose from Tosyl Cellulose

About 3 g of dry sodium iodide was dissolved in acetonyl-acetone (250 ml) in a conical flask and heated to 115-120°C using air condenser. To this, tosyl cellulose 3 g was added
and the reaction was continued for 7 hr with occasional vigorous shaking. Finally, the mixture was filtered and residue washed with methanol, (250 ml) and 0.1N sodium thiosulfate solution (500 ml). The material was removed from the filter, stirred twice with 250 ml portions of 0.1N sodium thiosulfate and finally washed on the filter to remove any adsorbed iodine. The product was washed with distilled water and then extracted with solvent ether in a soxhlet apparatus, and dried in a vacuum desiccator over P₂O₅. The D.S. of iodine for low and high D.S. tosyl cellulose samples was 0.11 and 0.69 respectively.

Iodotosyl Cellulose Acetate from Tosyl Cellulose Acetate

Tosyl cellulose acetate (5 g) and sodium iodide (10 g) were dissolved in dry acetonylacetone (80 ml). The mixture was refluxed for 3 hr at 120°, cooled and poured into 1 liter of iced water. The mixture was allowed to stand and filtered. The residue was washed with distilled water, dried and purified by reprecipitation from aqueous acetone. The product had the following analysis: D.S.(Acetyl), 1.92; (Tosyl), 0.29; (Iodine), 0.21.

Preparation of Tosylated Fabric

Tosylation of fabric was carried out by following the procedure described in Chapter IV for chlorination of fabric except that tosyl chloride was used as the reagent.
A fabric piece (12" x 28") was wound round the frame and wetted with pyridine. The fabric on the frame was then immersed in pyridine containing tosyl chloride. The proportion of cloth : tosyl chloride : pyridine was 1:10:50. The reaction was carried out at 25° for 15 days. After the reaction period, the fabric was removed from the roll, washed thoroughly in a pyridine-water mixture, washed in water, and soxhlet extracted in acetone and finally washed with water and dried; D.S.(Tosyl), 0.75.

A small piece of fabric was tosylated for 10 days only, in a small flask and given the same after treatment; D.S.(Tosyl), 0.53.

Tosyl Cellulose

After squeezing out excess benzene, the activated cotton slivers (20 g) were placed in a 1 liter, ground glass flask, pyridine (200 ml) was added, and the mixture was kept overnight at room temperature. A solution of tosyl chloride (235 g) in pyridine (250 ml), cooled to 10°, was added slowly during a period of 30 min at 5-10° with stirring. The flask was then placed in a water-bath (25°) and was shaken continuously. After 48 hr, the flask was removed from the bath, cooled in a ice-bath for 10 min, and acetone (225 ml) containing water (35 ml) at 0° was added to decompose the remaining tosyl chloride. The mixture was shaken for 10 min in ice-water and poured into distilled water (3 l).
The suspension was stirred for 1 hr after which it was filtered through a sintered glass funnel (G-3) and washed well with distilled water. The product was then suspended in distilled water overnight, collected by filtration and extracted with methanol and then with ether in a soxhlet apparatus. The sample was then air-dried at room temperature and finally dried in a vacuum desiccator over P₂O₅. D.S. (Tosyl), 1.1.

In a similar way a tosyl cellulose having low D.S. (0.17) was prepared by reacting activated cellulose with the reagents for 5 hr. The product was isolated by the method described as above.

Tosylation of Cellulose Acetate

Commercial, acetone-soluble cellulose acetate (10 g, D.S. 1.91) was dissolved in pyridine (60 ml), cooled to 20° and mixed with a solution of tosyl chloride (55 g) in pyridine (120 ml) at 20°, with shaking. The mixture was kept at 20° for 7 days with occasional shaking. After this period, it was poured into water (3 l) at 0° containing some acetone to decompose the excess of tosyl chloride. After stirring, the precipitate was filtered, washed well with water and dried. For further purification it was dissolved in acetone and reprecipitated, filtered and dried. D.S. (OAc), 1.91; D.S. (OTs), 0.56.
Trityl Cellulose

Regenerated cellulose (5 g, cellulose acetate saponified with 15% aqueous ammonia) was heated with 1:1 pyridine-water (100 ml) on a steam-bath for 1 hr. It was filtered and treated again in the same way with dry pyridine. After the last filtration, without letting the fibres become dry, it was suspended in dry benzene (100 ml) which was subsequently distilled. To the residue dry pyridine (100 ml) and trityl chloride (20 g, 2.25 moles) were added and the reaction continued on a steam-bath for 18 hr. The resultant dark colored solution, after dilution with pyridine and filtration, was precipitated with methanol (500 ml). The precipitate was washed with methanol till free from tritanol. The crude product was dissolved in dry pyridine and again precipitated, filtered and dried; D.S. (Trityl), 1.13.

6-0-Trityl 2(3)-p-Tolylsulfonyl Cellulose

To a solution of tritylcellulose (5 g) in dry pyridine (20 ml) was added a cold solution of p-tosyl chloride (21.2 g) in dry pyridine (17 ml) and the reaction was carried out at 20° for 10 hr with continuous stirring. The mixture was cooled to 0° and treated slowly with 3:1 acetone-water (250 ml, cooled to 0°). The mixture was brought to room temperature, then poured into methanol (500 ml). The fibrous precipitate was extracted with
methanol in a Soxhlet apparatus and then with ethyl-ether and dried. D.S.(Trityl), 1.13; D.S.(Tosyl), 0.86.

Potassium t-BuOK (t-BuOK)

To dry t-butyl alcohol (500 ml) in a 3 liter three-necked flask equipped with an efficient mercury sealed stirrer, a nitrogen inlet, a 500 ml dropping funnel with a pressure equalizing side tube and a reflux condenser there was added 20 g (0.5 g atom) of clean potassium metal. After the potassium had reacted, the condenser was replaced by a 12 inch distillation column and the excess t-butyl alcohol removed by distillation until crystals began to form in the solution. Dry heptane (2 l) was added and distillation continued until the head temperature reached 98°. The residual mixture was adjusted to 1.5 liter by addition of dry heptane and the resulting slurry of potassium t-butoxide in heptane was cooled to 0.5° in an ice-bath.

t-BuOK prepared in this manner was a 1:1 complex with t-butyl alcohol; neutralization equivalent calculated for this complex was 186. The complex can be isolated by simply removing the solvent at 20-25 mm pressure on a steam-bath. It can be stored for several months under a nitrogen atmosphere.
Dehydrohalogenation of Chlorodeoxy Cellulose and Its Acetate

Chlorodeoxy cellulose \( \sim 0.56 \text{ g, D.S.(Cl), 0.15} \) was treated with 9% methanolic KOH (10 ml) at 72° for 24 hr. The treated sample was washed with absolute methanol till free from alkali and then dried. Similarly, chlorodeoxy cellulose acetate \( \sim 1.5 \text{ g, D.S.(Cl), 0.25; acetyl, 1.35} \) was treated with 9% methanolic KOH (30 ml) at 72° for 24 hr. The product was poured into cold water, washed with methanol to remove alkali and dried.

Reaction of Chlorodeoxy Cellulose and Its Acetate with t-BuOK in DMSO

Chlorodeoxy cellulose \( \sim 1.71 \text{ g, 10 m.moles, D.S.(Cl), 0.25} \) was suspended in DMSO (10 ml) and t-BuOK \( \sim 3.72 \text{ g, 20 m.moles} \) dissolved in DMSO (20 ml) was added and the reaction mixture kept at room temperature for 20 hr. It was then poured into cold ethanol, and the fibrous solid thus obtained was centrifuged, washed with ethanol repeatedly and the ethanol displaced with solvent ether followed by petroleum ether and dried.

To a solution of chlorodeoxy cellulose acetate \( \sim 1 \text{ g, 4 m.moles, D.S.(Cl), 0.58; (Acetyl), 1.38} \) in DMSO (15 ml), t-BuOK (1.5 g or 8 m.moles) dissolved in DMSO (15 ml) was added and the reaction allowed to take place at room temperature for 1 hr. The product was poured over crushed ice and the
precipitated material washed with distilled water till free from alkali. It was finally washed with ethanol and dried.

In a similar manner chlorodeoxycellulose acetate $\left[0.91 \text{ g, 4 m.moles, D.S.} (\text{Cl}), 0.25; \text{ (Acetyl), 1.35} \right]$ in DMSO (15 ml) was treated with t-BuOK (1.5 g, 8 m.moles) in DMSO (15 ml) at 95° for 4 hr, and the product recovered as described above.

Reactions of Iodocellulose with t-BuOK/DMSO

Iodotosyl cellulose $\left[0.32 \text{ g, 1 m.mole, D.S.} (\text{Iodine}), 0.69; \text{ (Tosyl), 0.45} \right]$ in DMSO (3 ml) was reacted with t-BuOK (0.186 g, 1 m.mole and 0.75 g, 4 m.mole) in DMSO (7 ml) at room temperature for 2 hr. The products were isolated by pouring the mixture into cold water, filtration, washing with water and drying.

Reaction of Mesyl Cellulose with t-BuOK/DMSO

Mesyl cellulose (1 g, 5 m.moles, D.S. (Mesyl) 0.58$^-$) was suspended in DMSO (10 ml) and to the resulting mixture t-BuOK (1.86 g, 10 m.moles) in DMSO (20 ml) was added. The reaction was allowed to proceed at room temperature for 20 hr after which period the product was filtered, the residue washed thoroughly with methanol and then dried.
To tosyl cellulose acetate $1\, g, 3\, \text{m.moles, D.S. (Tosyl), 0.56; (Acetyl), 1.92}$, dissolved in DMSO (15 ml) was added t-BuOK (1.12 g, 6 m.moles) in DMSO (15 ml) and the reaction allowed to take place at 95° for 3 hr. The reaction product was poured over cold distilled water, centrifuged, washed several times with water and dried.

With a view to studying the effect of time on the extent of the reaction, the following experiment was carried out:

Tosyl cellulose acetate $5\, g, 15\, \text{m.moles, D.S. (Tosyl), 0.56; (Acetyl), 1.92}$ dissolved in DMSO (50 ml) was treated with t-BuOK (5.6 g, 30 m.moles) in DMSO (100 ml). At intervals of 5, 10, 24 and 28 hr, samples were drawn and poured over ice-cold distilled water. The precipitated material was recovered by centrifugation and then washed successively with distilled water, methanol, ethyl ether, petroleum ether and dried.

Reaction of Tosyl Cellulose with t-BuOK/DMSO

(i) Tosyl cellulose $0.66\, g, 2\, \text{m.moles, D.S. (Tosyl) 1.7}$ was suspended in DMSO (5 ml) and varying quantities $2, 4, 6, 8$ and $12\, \text{m.moles, i.e., 0.37 g, 0.74 g, 1.12 g, 1.5 g} \text{ and 2.2 g respectively of t-BuOK in DMSO (10 ml) were added. The reaction was allowed to proceed for 23 hr at room temperature on a mechanical shaker. The reaction product was}$
poured into cold methanol and the precipitated material (fibrous or powdery) was recovered by centrifugation followed by washing successively with methanol, ethyl ether and petroleum ether and drying.

(ii) Tosyl cellulose (0.66 g, 2 m.moles) in DMSO (5 ml) was treated as above with t-BuOK (0.372 g, 2 m.moles) in DMSO (10 ml) and the reaction allowed to take place at room temperature for 2, 7, 18 and 30 hr.

The different products were isolated by the method described above.

(iii) Similar experiments were carried out at 65° with time intervals of 0.25, 0.5, 1.0, 1.5 and 2.0 hr. The products were isolated as usual.

(iv) Tosyl cellulose (0.95 g, 5 m.moles, D.S. 0.17) was reacted with (5 and 20 m.moles, 0.93 g and 3.72 g) for 2 and 23 hr respectively, at room temperature and resulting products were isolated by the above procedure.

(v) Tosyl cellulose (D.S. 1.1) was taken in DMSO and potassium hydroxide solution (9%, dissolved in minimum quantity of methanol, and diluted with required volume of DMSO) was added. The reaction was carried out for 2 hr at room temperature and the product was isolated in the usual manner.
Reaction of Iododeoxy Cellulose with AgNO₃/DMSO

Iododeoxy cellulose \( \sim 0.1 \) g, D.S.(Iodine), 0.69; (Tosyl), 0.43 \( \approx \) was treated with AgNO₃ (0.25 g) in DMSO (5 ml) at 100° for 1.5 hr. The reaction mixture was poured over crushed ice, after cooling to room temperature, and the solid material collected by filtration was washed with cold distilled water, then with methanol and dried.

Reaction of Tosylated Fabric with t-BuOK/DMSO

Tosylated fabrics \( \sim \) D.S.(Tosyl), 0.53 and 0.75 \( \approx \) were reacted at room temperature with varying concentrations of t-BuOK (1, 2 and 4 molar proportions) in DMSO for 2,9 and 20 hr with continuous shaking. After the reaction period, the fabric pieces were washed thoroughly with distilled water, then acetone and dried.

Attempted Synthesis of 2,3-Cellulose

6-O-Trityl-2,3-di-O-tosyl cellulose \( \sim 0.59 \) g, 1 m.mole, D.S.(Trityl), 1.13; (Tosyl), 0.86 \( \approx \) in DMSO (5 ml) was treated with t-BuOK (0.186 g, 1 m.mole) in DMSO (10 ml) at 95° for 2 hr. The product was isolated by washing with cold distilled water, methanol and drying.
Addition Reactions Across the Double Bond

The addition reactions of chloroform were carried out as follows:

(i) Unsaturated fabric (0.2 g) was taken into a quartz glass test tube and filled with dry chloroform (3 ml) and closed. The mixture was then irradiated by UV light for 16 hr at 25°. At the end of the reaction, chloroform was decanted diethyl ether (5 ml) was added and the material was filtered through sintered glass funnel (G-3), repeatedly washed with ether and dried.

(ii) To unsaturated fabric (0.2 g) in chloroform was added benzoyl peroxide (0.02 g) and shaken vigorously for 2 min. Then the reaction was continued at room temperature on a mechanical shaker for varying length of time. After the reaction period, the fabric was filtered, washed thoroughly with dry chloroform, ether and dried.

Grafting Reactions

Ceric ammonium sulfate solution (50 ml, 0.006 N solution in 1% sulfuric acid) was taken in 100 ml Erlenmeyer flask and the flask was kept in a water bath (50°) to attain the temperature. To this was added freshly distilled acrylonitrile monomer (1 ml), followed by immediate addition of the sample to be grafted. The flask was well stoppered and
the contents stirred occasionally during the course of polymerisation. The reaction was carried out at this temperature for 3 hr, then the flask was removed from the bath, and sample was washed thoroughly with distilled water and then extracted with DMF in a Soxhlet apparatus for 24 hr. Then it was again washed with water and dried. The percentage graft was calculated by the increase in weight of the substrate and nitrogen content.

Hydrolysis

Acid hydrolysis was carried out by the method described in Chapter II. Some samples were also treated initially with cold (0°) 72% sulfuric acid for 3 to 5 hr.

For methanolysis, 0.5 g of the sample was treated with methanolic hydrochloric acid (5%; 5 mL) in a sealed tube at 120° for 16 hr. After cooling, the material was filtered, the residue washed with methanol and the filtrate was neutralized with silver carbonate, centrifuged and the supernatant filtered and concentrated. The mixture of methyl glucosides so obtained was investigated by paper chromatography. The residue was dried and weighed (0.47 g).

Enzymatic hydrolysis was carried out as follows:

Unsaturated cellulose having 19 double bonds (prepared from mesyl cellulose) and 33 double bonds (prepared from
tosyl cellulose) were taken in 50 ml. Erlenmeyer flasks and acetate buffer (30 ml) was added to each flask. Cellulase enzyme (20 mg) was then added and the flasks were kept at 45° for 10 days. Aliquots of 5 ml solution were taken from each flask at intervals of 3 days, filtered, and ethanol (20 ml) was added, again filtered and the solution was concentrated. The syrup gave spot corresponding to glucose only on paper chromatograms.

**Determination of Unsaturation**

Quantitative determination of unsaturation in cellulose derivatives was carried out by modified Siggia's method. It gave good results on some organic compounds containing double bonds. Some of the results obtained were compared with the results obtained by Maclini's method. The values were found to be nearly the same by both the methods.

The method involves the use of the following reagents:

- 0.05 N Brominating solution (Prepared by dissolving 0.695 g KBrO₃ and 2.5 g KBr in 500 ml water)
- 0.01 N Sodium thiosulfate solution
- Potassium iodide (solid)
- 1% Starch solution
- 10% Hydrochloric acid
Accurately weighed sample (10-50 mg) was taken in a 150 ml conical flask containing 4-5 small glass beads, and brominating solution (10 ml) was added. Then 1 ml of 10% hydrochloric acid was added and the flask was stoppered quickly, sealed with wax and covered with dark paper. Then it was shaken on a mechanical shaker for about 4 to 6 hr. After that, KI (about 1 to 1.5 g) was added and the liberated iodine was immediately titrated against sodium thiosulfate solution. When the solution became pale yellow, starch solution (2 to 3 ml) was added and the solution titrated to the end point. Similarly, a blank experiment was run without the sample. The difference in the two titration readings indicated the consumption of iodine, which was related to the bromine consumed by the unsaturated compound. The theoretical bromine number and number of double bonds were calculated by the following formulae:

Theoretical bromine number = \( \frac{159.8 \times 100}{\text{mol.wt. of basic unit}} \)

No. of double bonds/100 GPU = \( \frac{\text{Actual bromine number} \times 100}{\text{Theoretical bromine number}} \)
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