Preparation of Cellulose Derivatives via Ring-Opening Reactions with Cyclic Reagents in Lithium Chloride/ N,N-Dimethylacetamide

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ABSTRACT: Reactivity of cellulose hydroxyl functional groups to strained-ring systems was examined in the lithium chloride/N,N-dimethylacetamide solvent. Epoxide reagents were unreactive to cellulose hydroxyl groups in nucleophilic ring-opening reactions. Cyclic anhydrides and lactones readily reacted in the presence of triethylamine, while 1,3-propane sultone reacted with the competing chloride anion in the DMAc/LiCl solvent. ϵ-Caprolactone reacted with cellulose to form a hydroxy-terminal ester derivative by an addition-elimination mechanism. A novel cyclic iminium chloride cellulose derivative and subsequent hydrolysis products were prepared.

Introduction

The polar aprotic nature of the lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) solvent allows a range of organic reactions including typical alcohol modification reactions such as esterification and carbamate formation. The cellulose molecule contains three hydroxyl groups per anhydroglucose residue (AGR), and each of these (one primary, OH(6), and two secondary, OH(2) and OH(3)) can react in the same manner as low molecular weight substances of similar composition.[1]

Previous research in our laboratories has resulted in the synthesis of a large number of cellulose derivatives using the LiCl/DMAc solvent. The preparation of cellulose esters and carbamates is facile utilizing acid chlorides and isocyanates,[2] respectively. Cellulose has been reacted as well with toluenesulfonyl chloride in LiCl/DMAc to produce the sulfonate ester.[3] Acid chlorides, isocyanates, and sulfonyl chlorides, having high ground-state potential energies, are readily attacked by nucleophilic, hydroxyl functional groups under mild conditions. Typically these reactions are conducted at room temperature using a tertiary amine (pyridine or triethylamine) which performs as an acid scavenger for the acid chloride reactions, as a catalyst with the isocyanate reactions, and as an activator/H^+ scavenger in the sulfonyl chloride reaction.

The reaction of cellulose with epoxide reagents can be used to prepare cellulose ethers in LiCl/DMAc.[2,4] This typically requires high temperatures, long reaction times, and strongly alkaline conditions. As a result, considerable polymer degradation results. Cyclic anhydrides, however, have been used to prepare cellulose monoesters from maleic, succinic, and phthalic anhydride in the presence of potassium acetate at 100 °C.[5] Another ring-opening derivatization is the reaction of lactide (3,6-dimethyl-1,4-dioxane-2,5-dione) with cellulose, yielding cellulose 2-(2-hydroxy-1-oxopropoxy)propanoate with DS = 1.4.[6]

In this work, we examine reactions of a range of cyclic reagents with cellulose in homogeneous solutions of lithium chloride and N,N-dimethylacetamide (LiCl/DMAc).

Experimental Section

Materials. Purified, reagent grade cellulose used in this study was obtained from J. T. Baker Chemical Co., cat. no. 1529. This material[4] is microcrystalline with $M_w = 1.5 \times 10^5$; no information about polydispersity is available. Other reagents were used without further purification unless specifically noted.

LiCl/DMAc Solvent. Stock solutions of LiCl in DMAc (9% w/w) were prepared by dissolving 4.2 g of reagent grade lithium chloride (Aldrich) in 50 mL of N,N-dimethylacetamide (Aldrich) at 80 °C. Solvent mixtures for each experiment were prepared immediately prior to use to minimize moisture uptake.

Cellulose Preparation. The cellulose was pretreated as follows to facilitate dissolution: Cellulose powder (100 g) was slurried overnight in 500 mL of deionized water. The mixture was vacuum filtered over coarse fritted glass. The cellulose was then added to 500 mL of reagent grade methanol, stirred for 1 h, and filtered. This procedure was repeated three times. Five similar repetitions with 500 mL of DMAc completed the process. The concentration of cellulose per gram of swollen material was determined by drying several 1.0-g samples in a vacuum oven at 80 °C for 48 h. The average cellulose content for this material was thus determined to be 0.486 g/g of sample.

Cellulose Dissolution. Fresh LiCl/DMAc solvent was prepared as described above in a dry, 100-mL, three-necked flask equipped with a dry nitrogen inlet/outlet, heating mantle, thermometer, and magnetic stirrer. After the temperature was allowed to reach 80 °C, 1.0 g of solvent-exchanged cellulose (0.486 g of actual cellulose weight or 9.0×10^{-3} mol of hydroxyl functionality) was added to the heated solvent. The mixture was allowed to stir with nitrogen sparging while cooling to room temperature. Complete cellulose dissolution was apparent at 40–50 °C or after ca. 20 min. All subsequent reactions were performed under a nitrogen atmosphere.

Synthesis. Epoxides. A number of reactions of 1,2-epoxypropane and 1,2-epoxybutane with cellulose were attempted utilizing a number of catalysts. Among these were $ZnCl_2$, H_2SO_4, and Al_2O_3. No evidence of reaction was observed.

Anhydrides. (a) Monomethyl Succinate Model Compound (Method of Cason).[7] To a 250-mL, three-necked, round-bottom flask were charged succinic anhydride (40 g, 0.334 mol) and 20 mL (0.494 mol) of reagent grade methanol. The flask was placed in a steam bath, and the solution was refluxed for 1.5 h. The purified half-ester melted at 54 °C (lit. mp 56–59 °C). IR (cm^{-1}): C=O, 1750 and 1710; OH (br) 3500. ^{13}C NMR (ppm): C=O(ester), 175.6; C=O(acid), 177.3; CH_3, 53.8; CH_2, 31.0 and 31.2.

(b) Monomethyl Succinate Model Reaction in LiCl/DMAc. To a 250-mL, round-bottom flask were added 40 g (0.334 mol) of succinic anhydride, 20 mL (0.494 mol) of methanol, and 50 mL of 9% LiCl/DMAc. The flask was placed in a steam bath and the solution was refluxed for 5 h. The isolated product was identical with that from the previous experiment. The melting point was 55 °C. IR (cm^{-1}): C=O, 1750 and 1710; OH (br), 3500. ^{13}C NMR (ppm): C=O(ester), 175.1; C=O(acid), 176.8; CH_3, 53.5; CH_2, 31.0 and 31.2.

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(c) Cellulose Monoester of Succinic Acid (with Na_2CO_3). To a 50-mL, three-necked flask were charged 25 mL of 9% LiCl/DMAc and 0.5 g of solvent-exchanged cellulose (0.24 g of dry cellulose, 5.42×10^{-3} mol of OH functionality). After formation of a clear solution, 0.9 g (8.0×10^{-3} mol) of Na_2CO_3 was added to the reaction mixture, and the temperature was raised to 120 °C. A solution of 1.6 g (1.6×10^{-2} mol) of succinic anhydride in 10 mL of DMAc was added dropwise to the reaction mixture. The mixture became colored soon after complete addition. The color darkened from light pink to deep purple. Fifteen minutes after the first addition of anhydride, an aliquot of the reaction mixture was pipetted into ~5 mL of water and found to be water soluble. The protonated product was acetone soluble, and the salt form was water soluble. The reaction was allowed to continue for a total of 30 min at 120 °C. The heat was removed, and the mixture was filtered, precipitated into acetone, and dried in a vacuum oven at room temperature. IR (cm^{-1}): C=O, 1738 and 1710; OH (br), 3500. ^{13}C NMR (ppm): C=O(acid, Na^+), 183.7; C=O(acid, H^+), 177.8; C=O(ester), 163.5; CH_2, 35.0 and 33.2; cellulose peaks, 105–63.

(d) Cellulose Monoester of Succinic Acid (with Pyridine). A solution of 1.0 g of solvent-exchanged cellulose (9.0×10^{-3} mol of OH functionality) in 50 mL of 9% LiCl/DMAc was prepared in a 100-mL, three-necked flask. To the cellulose solution was added 3.0 mL (3.7×10^{-2} mol) of pyridine. The solution was then heated to 80 °C. A solution of 3.2 g (3.2×10^{-2} mol) of succinic anhydride was added dropwise to the reaction mixture. After 2.5 h, the polymer was precipitated into tetrahydrofuran (THF). The product was dissolved in deionized water and precipitated by addition of 0.1 N HCl. After drying, the yield was 0.91 g. The protonated product was acetone soluble, and the salt form was water soluble. This yield corresponds to a DS = 1.4 of the protonated acid substituent. IR (cm^{-1}): C=O, 1730 and 1710; OH (br), 3500. ^{13}C NMR (ppm): C=O(acid, Na^+), 184.0; C=O(acid, H^+), 178.1; C=O(ester), 163.1; CH_2, 35.0 and 33.6.

(e) Cellulose Monoester of Succinic Acid (with Triethylamine (TEA)). Succinic anhydride (2.8 g, 2.8×10^{-2} mol) was added to 50 mL of a 1.0 wt% solution of cellulose in 9% LiCl/DMAc in a 100-mL, three-necked flask. With the reaction mixture at room temperature, TEA (4.0 mL, 2.9×10^{-2} mol) was added by pipet. Within 5 min of addition, the polymer precipitated. The reaction mixture was filtered, and the polymer was dissolved in 50 mL of deionized water. The product was precipitated by addition of 0.1 N HCl. The polymer was redissolved in a $NaHCO_3$ solution. Additional $NaHCO_3$ was added to achieve pH 8. The polymer was then precipitated in acetone and dried. The protonated product was acetone soluble, and the salt form was water soluble. The yield of 0.89 g suggested a DS = 1.1 of the Na^+ salt. The protonated polymer decomposed at 180 °C. IR (cm^{-1}): C=O 1732 and 1710; OH (br) 3500. ^{13}C NMR (ppm): C=O(acid, Na^+), 183.7; C=O(acid, protonated), 177.9; C=O(ester), 163.0; CH_2, 34.7 and 33.2; cellulose backbone peaks, 62–105.

(f) Cellulose Monoester of Maleic Acid. Maleic anhydride (MA, 2.7 g, 2.8×10^{-2} mol) was added to 50 mL of 1.0 wt % cellulose in 9% LiCl/DMAc in a 100-mL, three-necked flask. With the reaction mixture at room temperature, TEA (4.0 mL, 2.9×10^{-2} mol) was added. After 3 min the polymer precipitated. After collection, the polymer was dissolved in 50 mL of deionized water and reprecipitated into acetone. The protonated product was acetone soluble, and the salt form was water soluble. The product was dried in a vacuum oven at room temperature. The yield of 1.22 g indicates a DS = 1.2 of the TEA salt. IR (cm^{-1}): C=O (br), 1745; OH (br), 3500. ^{13}C NMR (ppm): C=O(acid, H^+TEA), 176.9; C=O(ester), 168.8; CH(vinyl), 145.1 and 120.7; cellulose backbone peaks, 105–62.

Sultone. (a) 3-Chloro-1-propanesulfonate. LiCl (2.1 g, 5.0×10^{-2} mol) was dissolved at 80 °C in 25 mL of DMAc in a 50-mL, three-necked flask. The solution was allowed to cool to room temperature. 1,3-Propane sultone (3.1 g, 2.6×10^{-2} mol) was added in bulk to the solution. A temperature increase of ~10 °C resulted. An aliquot of the reaction mixture was taken for ^{13}C NMR analysis. Chemical shifts of the ring-opened product were noted. ^{13}C NMR (ppm): CH_2, 51.5, 47.6, and 31.8. This compares to the sultone ring CH_2 shifts of 73.1, 47.2, and 26.8 ppm.

(b) 3-Bromo-1-propanesulfonate. LiBr (4.3 g, 3.4×10^{-2} mol) was dissolved at 80 °C in 25 mL of DMAc in a 50-mL, three-necked flask. After the solution was allowed to cool to room temperature, propane sultone (3.1 g, 2.6×10^{-2} mol) was added. The temperature increased to 42 °C. An aliquot of the reaction mixture was taken for ^{13}C NMR analysis. The chemical shifts of the ring-opened product were recorded. ^{13}C NMR (ppm): CH_2, 52.4, 46.9, and 31.9 ppm.

Lactone. (a) Cellulose 6-Hydroxycaproate. A 50-mL, three-necked flask was charged with 50 mL of 1.0 wt % cellulose in 9% LiCl/DMAc, triethylamine (4.1 mL, 2.9×10^{-2} mol), and ε-caprolactone (3.0 mL, 2.7×10^{-2} mol). The temperature was raised to 80 °C. After 18 h, the polymer was precipitated into acetone. The product (0.75 g, ca. DS = 0.8) was soluble in DMSO. A broad melting range was noted at ca. 170 °C with decomposition near 200 °C. IR (cm^{-1}): C=O, 1744; OH (br) 3500. ^{13}C NMR (ppm): C=O, 173.6; CH_2, 61.2, 33.9, 32.3, 25.9, and 24.7; cellulose backbone peaks, 103–62.

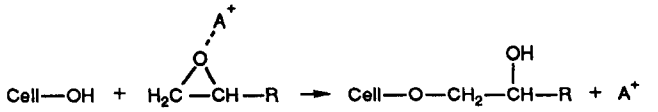
Pyrrolidinone. (a) (1-Methyl-1-pyrrolin-2-yl)cellulose Chloride. Pyridine (1.4 mL, 1.7×10^{-2} mol) was added to 25 mL of 1.0 wt % cellulose in 9% LiCl/NMP in a 50-mL, three-necked flask. A solution of tosyl chloride (3.4 g, 1.8×10^{-2} mol) in 5 mL of DMAc was added dropwise to the reaction mixture. After 12 h the product was precipitated into THF. The polymer was soluble in water and methanol. The product was found to decompose at 170 °C. IR (cm^{-1}): C=N, 1640. ^{13}C NMR (ppm): C=N, 182.0; CH_2, 57.4, 36.0, and 19.9. The absorption at 1746 cm^{-1} is likely due to hydrolysis (next section).

(b) Cellulose 4-(Methylamino)butyrate Hydrochloride. The product of the above reaction was hydrolyzed in D_2O; the hydrolysis was monitored by ^{13}C NMR. These spectra indicated that the hydrolysis product was the ring-opened derivative. The peaks attributed to the iminium species decreased in intensity with time. Peaks that increased in intensity with time were assigned to the opened ring. IR (cm^{-1}): C=O, 1746; NH, 2810. ^{13}C NMR (ppm): C=O, 177.2; CH_2, 50.8, 35.5, and 23.3. This polymer remained in solution even after several days.

Results and Discussion

After our initial reactions of cellulose in DMAc/LiCl, we had anticipated facile formation of other derivatives under homogeneous reaction conditions. However, the reactivity of cellulose hydroxyl groups in S_N2 or A_2 displacement reactions in LiCl/DMAc has thus far been insufficient to result in reasonable yields. Epoxide ring-opening reactions and simple alkylation reactions, for example, have yielded low degrees of substitution and considerable polymer degradation. The limited nucleophilicity of the cellulose hydroxyl groups (and low ground-state potential energy) requires the use of alkaline reaction conditions in order to produce the more reactive cellulose alkoxide anion.

Epoxides. Preferring to maintain homogeneous, nondegrading conditions, we attempted to enhance the susceptibility of the epoxy ring to attack by the hydroxyl groups. Toward this end, Lewis acids and protic acids were able to lower the activation energy for ring opening as shown in eq 1, where A represents either a Lewis acid or H^+. No evidence of epoxide reaction was noted

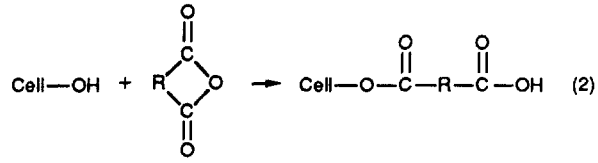


(1)

for any of the syntheses attempted. The results of these experiments support our previous contention that etherification of cellulose in the LiCl/DMAc solvent holds no advantage over current heterogeneous methods.[4]

Anhydrides. Another ring-opening reaction of interest is that of cellulose with cyclic anhydrides as illustrated in

eq 2. Reactions of this type produce half-acid esters.



Classically, these reactions have been carried out heterogeneously on cotton fabrics or regenerated cellulose at 150–160 °C and have resulted in DS values of 0.13–1.08.[8-10] The products generally displayed increased moisture retention and in few cases (DS > 0.5) were water soluble.[10]

Our first attempted reactions to produce cellulose half-acid esters in the LiCl/DMAc solvent system were uncatalyzed and utilized succinic anhydride. No reaction was observed at temperatures up to 80 °C for 12 h. In order to determine the LiCl/DMAc solvent interference with the esterification process, a model reaction was performed. Methanol was chosen as the model alcohol since its low boiling temperature (65 °C) would allow the reaction to be conducted within the temperature range of our previous cellulose experiments (60–80 °C).

The reaction mixture containing succinic anhydride and an excess of methanol in 9% LiCl/DMAc was refluxed for 90 min. The resulting product has a ^{13}C NMR spectrum and melting point matching those reported for the monomethyl succinate.[11] This evidence confirms that the anhydride ring can be opened by an alcohol in the presence of, and without interference from, the LiCl/DMAc solvent. It can be inferred from these results that the lack of reactivity of cellulose is largely due to steric restrictions of the hydroxyl functional groups.

At elevated temperatures (>80 °C), polymer degradation is evidenced by a darkening of the reaction mixture. Although the anhydride ring opens, subsequent acid-catalyzed cleavage of the cellulose glycosidic linkage likely results.

In order to minimize polymer degradation, sodium carbonate (Na_2CO_3) can be slurried into the reaction mixture. Water-soluble derivatives are produced at 80 °C after 20 h. Higher temperatures (85, 90, and 120 °C) result in reduced reaction times required to produce water-soluble cellulosics (12.5, 2.0, and 0.25 h, respectively). The ^{13}C NMR spectra of these products show the expected two carbonyl resonances of the ester and acid functionalities at 163 and 177 ppm, respectively (Figure 1).

When pyridine was used, the reaction temperature was reduced to 80 °C with a reaction time of 3 h. The resulting product was a white, water-soluble powder with a DS = 1.4. Later, triethylamine (TEA) was used as an activator/H^+ scavenger. Water-soluble cellulosics were prepared in <10 min at room temperature (DS = 1.1). This reaction provides an exception to most reactions in the LiCl/DMAc solvent. As mentioned previously, most cellulose derivatives remain soluble in the LiCl/DMAc system. TEA salts, however, are insoluble in this solvent. As a result, this reaction proceeds until the polymer precipitates. The limiting DS is, in this case, determined by the solubility of the TEA salt of the cellulose half-acid ester.

Maleic anhydride was also reacted with cellulose in the presence of TEA. Precipitate formation was noted to be even more rapid (~2 min) than with succinic anhydride. This water-soluble product (DS = 1.2) represented the first successful effort to introduce a pendent site of unsaturation onto the cellulose molecule in the LiCl/DMAc solvent.

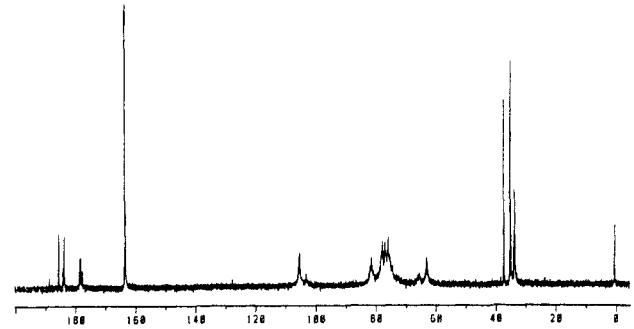


Figure 1. ^{13}C NMR spectrum of cellulose monoester of succinic acid.

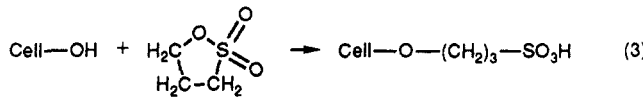
Table I
^{13}C NMR Chemical Shifts (ppm) for 3-Halo-1-propanesulfonate[a]

	carbon no.		
	1	2	3
LiCl	51.5	31.8	47.6
LiBr	52.4	31.9	46.9

[a] Chemical shifts are reported relative to 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS).

Although no other amines were studied, a tertiary amine with properties intermediate to those of TEA and pyridine may lead to lower temperatures and better control of reactivity. (Dimethylamino)pyridine may be such a reagent.

Sultones. The reactivity of anhydride reagents encouraged us to pursue preparation of similar derivatives with sulfonic acid groups through the ring opening of 1,3-propane sultone. An additional incentive for the use of this reagent was the possibility of preparing cellulose ether linkages (eq 3).

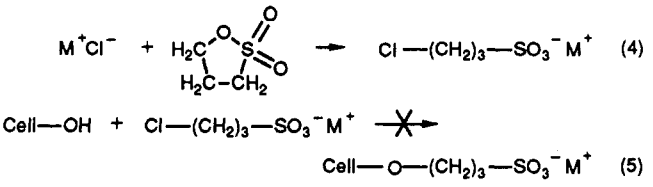


Derivatization of cellulose with propane sultone was not achieved in LiCl/DMAc. Analysis of the reaction mixture by ^{13}C NMR indicated that the sultone ring had opened; however, no evidence of a cellulose substitution reaction was found. NMR observation of the 1,3-propane sultone indicated that the LiCl/DMAc solvent had induced ring opening at room temperature. Preliminary indications were that the chloride ion attacked the sultone ring in preference to the cellulose hydroxyl group. The enhanced nucleophilicity of dissociated anions in polar aprotic solvents is well documented.[12]

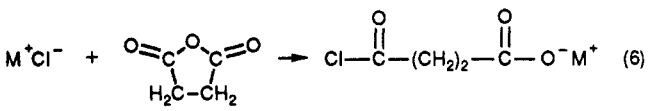
Ring Stability Comparison (Sultone versus Anhydride). To confirm that the chloride ion was the interfering nucleophile, we dissolved the sultone in neat DMAc and monitored the reaction by ^{13}C NMR with increasing temperature. The sultone ring remained intact even at 120 °C. Addition of LiCl to the sultone/DMAc solution, however, resulted in immediate opening of the ring. Substitution of LiBr for LiCl produced the same results with notable shifts in the product ^{13}C spectrum, confirming the involvement of the halogen in the reaction (Table I).

Attack of Cl^- on carbon 3 of the sultone ring produces the ring-opened 3-chloro-1-propanesulfonate (eq 4). This newly formed compound has an alkyl halide reactive site. In principle, S_N2 displacement of Cl^- by the cellulose hydroxyl could result in formation of the sulfonate derivative

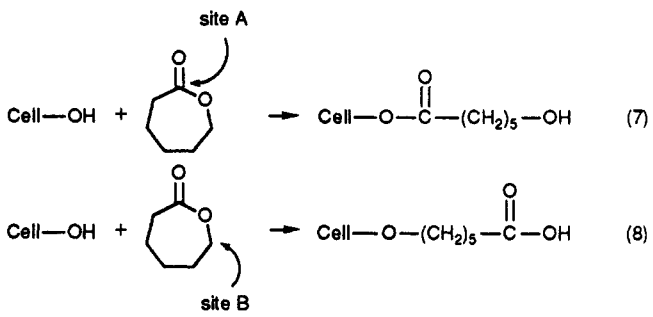
(eq 5). Such a reaction was never observed, consistent with other attempted alkylations and likely due to the low nucleophilicity of the cellulose hydroxyl groups.



The nucleophilicity of the chloride anion in LiCl/DMAc suggested that an alternative mechanism (eq 6) to classical anhydride ring opening might be occurring. However, an investigation of the stability of the anhydride ring in LiCl/DMAc using ^{13}C NMR demonstrated no evidence for an intermediate acid chloride.

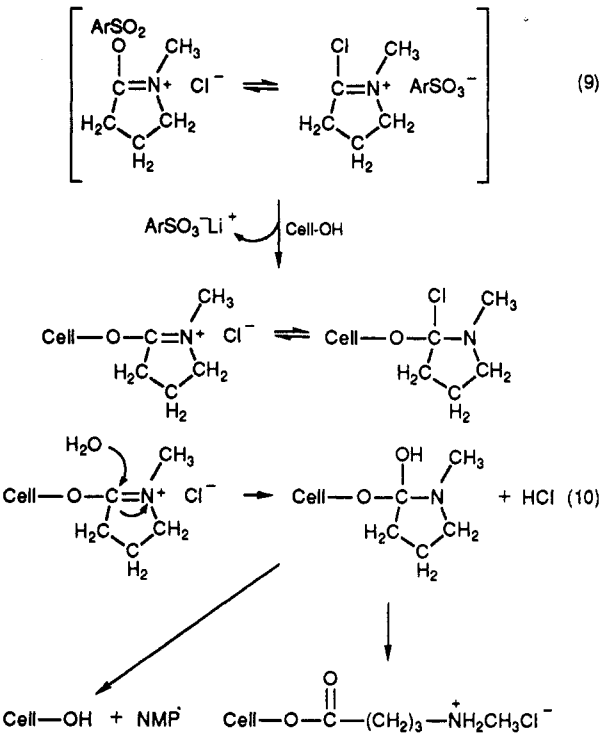


Lactones. Reaction of an anhydride reagent involves attack by the hydroxyl group on the carbonyl carbon to form the ester (eq 1). The mechanism likely proceeds through a tetrahedral intermediate. Nucleophilic attack of the hydroxyl group in the ring carbon, C-3, of propane sultone, on the other hand, occurs with nucleophilic displacement of the sulfonate group (eq 3). Of interest was the reaction pathway for a reagent providing sites for both mechanisms. Lactones provide such models. Nucleophilic attack of the cellulose hydroxyl group on the ϵ-caprolactone ring could, in principle, follow either of two routes: (1) attack at the carbonyl site A (eq 7) to produce the ester linkage and a terminal hydroxyl group or (2) attack on the ring carbon next to the heteroatom site B (eq 8) yielding an ether linkage and a terminal carboxylic acid.



If the lactone were susceptible to attack at site B, reaction with Cl^- might result in simple ring opening with no cellulose substitution (as observed with propane sultone). However, attack at the carbonyl carbon, site B (whether by Cl^- or by the cellulose OH), would result in esterification. Interestingly, the reaction of cellulose with ϵ-caprolactone in LiCl/DMAc yielded the cellulose ester shown in eq 7. The reaction was conducted at 80 °C in the presence of triethylamine. There is a marked decrease in reactivity as compared to the anhydrides, likely a reflection of the poor leaving group character of the alkoxide anion in comparison to the carboxylate anion. The resulting derivative was found to be DMSO soluble and water insoluble. After 18 h of reaction time, the level of substitution remained low (DS = 0.8). This low DS probably accounts for the water insolubility of the product.

Pyrrolidinone. In a previous paper we described the competitive formation of cellulose tosylate and cellulose deoxychloride proceeding via Vilsmeier–Haack reaction.[14] Further work in our laboratories has led to discovery of a novel reaction of cellulose with a cyclic intermediate reagent of a Vilsmeier–Haack type reaction of *N*-methylpyrrolidinone with toluenesulfonyl chloride. This reaction likely proceeds via an ionic intermediate which further reacts with cellulose, leading to a cyclic iminium chloride (eq 9). Subsequent hydrolysis of this derivative could follow two possible pathways shown in eq 10. One



route would regenerate *N*-methylpyrrolidinone and the underivatized cellulose. Alternatively, the ring could open, producing an ester linkage and the salt of a secondary amine. Evidence from ^{13}C NMR observations supports the latter case. This hydrolysis occurs much more rapidly than does that of the similar *N*,*N*-dimethylacetamide derivative. The iminium carbon resonance at 182.0 ppm disappears rapidly with the simultaneous appearance of the ester carbonyl at 177.2 ppm. The progression of this hydrolysis is followed in Figures 2 and 3. Although the upfield signal shifts are more subtle, the resulting peaks correlate well with calculated values for the opened ring (Table II). The hydrolysis product from this reaction remains water soluble.

Conclusions

The insufficient nucleophilicity of the cellulose hydroxyl groups in displacement reactions in LiCl/DMAc has been previously demonstrated with alkyl halides and epoxides.[4] In this study, further experiments using epoxides and various catalysts have reinforced this contention.

Cyclic anhydride reagents were successfully used to derivatize cellulose. With pyridine, the cellulose half-acid ester of succinic anhydride was synthesized in <3 h at 80 °C. Substitution of TEA for pyridine resulted in ambient temperature reactions with reaction times reduced to <10 min. Similar results were found with maleic anhydride. Both reagents produced water-soluble products.

The chloride ion has been proven to be a competitive nucleophile in the LiCl/DMAc solvent. Attempted ring

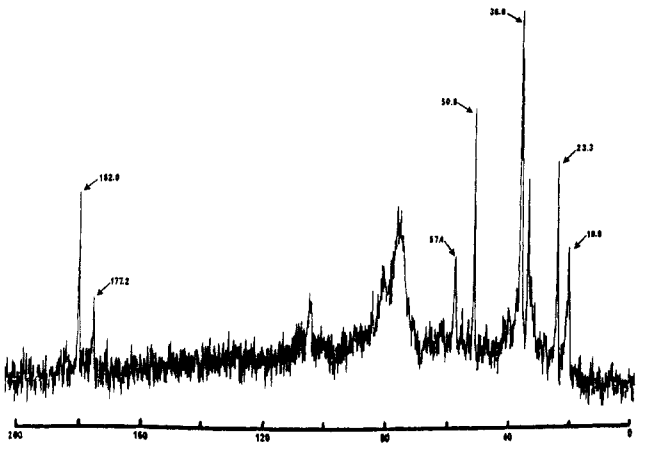


Figure 2. ^{13}C NMR spectrum of (1-methyl-1-pyrrolin-2-yl)-cellulose chloride.

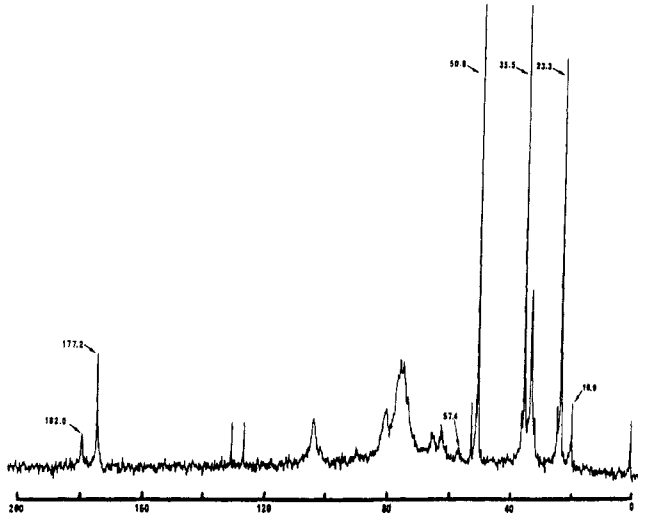


Figure 3. ^{13}C NMR spectrum of cellulose 4-(methylamino)-butyrate hydrochloride.

opening of 1,3-propane sultone with cellulose hydroxyl groups resulted in the ring-opened chloride product.

The ring opening of ϵ-caprolactone resulted in formation of a hydroxy-terminal ester derivative of cellulose. No evidence of a carboxylate resulting from an S_N2 attack on the lactone was detected. This demonstrates the preference for the cellulose hydroxyl group to add to the carbonyl bond with subsequent elimination in the LiCl/DMAc solvent.

Table II
^{13}C Chemical Shifts (ppm) for the Substituent Carbons of Cellulose 4-(Methylamino)butyrate Hydrochloride in D_2O[a]

	carbon no.			
	1	2	3	4
obsd	50.8	35.5	33.2	23.3
calcd	51.0	34.5	32.0	26.7

[a] Chemical shift calculations are based on additive shift parameters reported in ref 13.

Substituting LiCl/NMP as the solvent and utilization of tosyl chloride to form a Vilsmeier–Haak type of reactive intermediate led to the synthesis of (1-methyl-1-pyrolin-2-yl)cellulose chloride. Hydrolysis of this cyclic, iminium substituent produced cellulose 4-(methylamino)-butyrate hydrochloride—a new water-soluble cellulosic.

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