

New Procedure for the Preparation of Cellulose Esters with Aromatic Carboxylic Acids

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Esterification of cellulose with substituted or unsubstituted benzoic acids in the system of pyridine containing methanesulfonyl chloride at various reaction conditions was investigated. Cellulose could be readily acylated with 2-nitro-, 3-nitro-, 4-nitro-, and 4-azidobenzoic acids to form: *O*-(2-nitrobenzoyl)cellulose (DS = 3), *O*-(3-nitrobenzoyl)cellulose (DS = 3), *O*-(4-nitrobenzoyl)cellulose (DS = 2), and *O*-(4-azidobenzoyl)cellulose (DS = 1), respectively. In the case of benzoic acid, the mixed ester *O*-benzoyl-*O*-(methanesulfonyl)cellulose with DS \approx 0.9 was prepared. ¹³C NMR spectroscopy analysis was performed on hydrolyzed samples in DMSO. All products were characterized by both elemental and FTIR analyses. The derivatives are partially soluble in usual organic solvents, such as dimethyl sulfoxide and chloroform.

The chemical modification of cellulose, with various esterifying and etherifying agents, represents a widely practiced industrial technology worldwide. The reactions of cellulose under heterogeneous and homogeneous reaction conditions in which the hydroxyl groups are freely accessible have been described in many papers [1–4].

Incompletely modified cellulose derivatives, with regular substituent distribution along the backbone, irrespective of differences in accessibility due to morphology, are produced by peracylation followed by partial hydrolysis [5, 6].

Organic esters of cellulose can be prepared by the use of carboxylic acid anhydride with an acid catalyst [3, 7], carboxylic acid chloride in the presence of a base [3, 8, 9], isocyanates [3], and carboxylic acid in combination with trifluoroacetic anhydride [10]. Acid chlorides, isocyanates, and sulfonyl chlorides are readily attacked by nucleophilic, hydroxyl functional groups under mild conditions. Typically these reactions are conducted at room temperature using a tertiary amine (pyridine (Py) or triethylamine) [4].

In the work [11], Py—tosyl chloride—acetic acid system was used for the preparation of cellulose acetate. This method can be generally applied to the esterification with higher aliphatic and benzoic acids [12] or with substituted benzoic acids [13].

In this paper we describe a new synthesis of highly substituted esters of cellulose in pyridine using methanesulfonyl chloride (MsCl) instead of tosyl chloride.

EXPERIMENTAL

Microcrystalline cellulose powder with the polymerization degree $\overline{DP} = 160$ and $\overline{M}_m = 26000$ g mol⁻¹ (determined by viscometry measurements) was used as a cellulose sample. The substituted and unsubstituted benzoic acids were commercial products (Merck) and other used chemicals were of anal. grade purity.

The IR spectra were measured in KBr pellets using a PU 9800 FTIR device (Philips Analytical). The ¹³C NMR spectra of the derivatives were measured with a Bruker AM-300 device in DMSO-*d*₆ solutions with TMS as internal standard at 6000 Hz per point digital resolution. The samples before the NMR measurements were hydrolyzed under reflux at 100°C for 2 h.

Cellulose Esters with Substituted and Unsubstituted Benzoic Acids

0.3 g of cellulose dried at 105°C for 3 h was introduced into 25 cm³ of anhydrous pyridine and the mixture was stirred at room temperature for 30 min. Subsequently equimolar amount of substituted or unsubstituted benzoic acid (0.018 mol) and MsCl (2.1 g; 0.018 mol) were added into the solution. After reacting at 50°C for 0.5–5.0 h, the reaction mixture was poured into an excess of ethanol (150–200 cm³). The products were filtered off, washed with ethanol and finally extracted in a Soxhlet apparatus with ethanol for 6 h, then dried at 50°C for 2 h. The derivatives

Table 1. Modification of Microcrystalline Cellulose with Substituted and Unsubstituted Benzoic Acids in the Pyridine—Methanesulfonyl Chloride Mixtures

Compound	Reaction time h	DS	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$		
			C	H	N
<i>I</i>	0.5	0.4	47.65 47.84	5.05 4.84	2.53 2.57
<i>II</i>	1.0	0.6	48.69 48.86	4.69 4.62	3.34 3.47
<i>III</i>	2.0	1.3	50.94 50.61	3.91 3.97	5.12 5.17
<i>IV</i>	3.0	3.0	53.20 53.33	3.20 3.19	6.89 6.78
<i>V</i>	0.5	0.3	47.02 47.23	5.27 5.20	2.03 2.07
<i>VI</i>	1.0	0.4	47.65 47.16	5.05 5.07	2.53 2.68
<i>VII</i>	2.0	1.2	50.70 50.60	3.99 4.17	4.93 4.98
<i>VIII</i>	3.0	3.0	53.20 53.31	3.20 3.92	6.89 6.52
<i>IX</i>	0.5	0.6	48.69 48.08	4.69 4.86	3.34 3.63
<i>X</i>	1.0	0.9	49.85 49.92	4.29 4.48	4.26 4.32
<i>XI</i>	3.0	2.0	52.17 51.85	3.48 3.61	6.09 6.27
<i>XII</i>	5.0	2.0	52.17 51.96	3.48 3.52	6.09 6.02
<i>XIII</i>	3.0	1.0	50.81 50.63	4.23 4.20	13.68 13.86
<i>XIV</i>	3.0	0.9	56.49 56.58	5.23 5.38	1.21* 1.31*

Microcrystalline cellulose modified with: 2-nitrobenzoic acid (compounds *I—IV*), 3-nitrobenzoic acid (*V—VIII*), 4-nitrobenzoic acid (*IX—XII*), 4-azidobenzoic acid (*XIII*), and benzoic acid (*XIV*). * $w_i(\text{calc.})$ and $w_i(\text{found})$ for content of sulfur. **DS - degree of substitution by methanesulfonyl groups.

were characterized by elemental analysis and FTIR spectroscopy. The samples before ^{13}C NMR measurements (DMSO- d_6) were hydrolyzed by 2 M-TFA at 100°C for 2 h.

RESULTS AND DISCUSSION

By the preparation of esters of microcrystalline cellulose, substituted benzoic acids (2-, 3-, or 4-nitro-) as well as benzoic acid were used as reactants in amounts corresponding to the mole ratio 3.33:1 of a reactant to the OH groups of cellulose, and equimolar to the amount of MsCl. As can be seen from the results in Table 1, DS of the derivatives can be controlled by the reaction time 0.5–5 h at 50°C. By the modification of the cellulose with 2-nitro- and 3-nitrobenzoic acids within 3 h, the corresponding products *O*-(2-nitrobenzoyl)cellulose (*IV*) and *O*-(3-nitrobenzoyl)cellulose (*VIII*), respectively, with DS = 3 were prepared. The dependence of DS on the

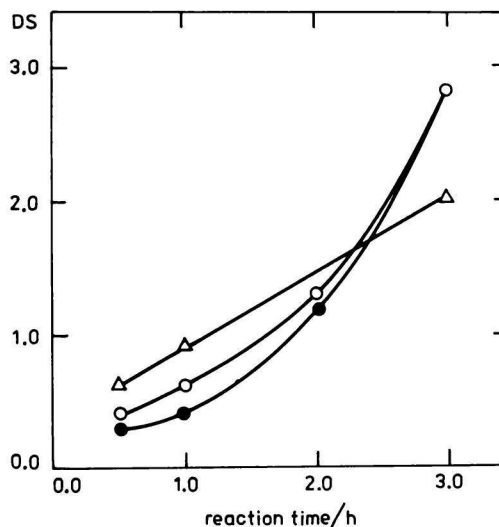


Fig. 1. The rate of esterification of cellulose with pyridine—methanesulfonyl chloride—substituted benzoic (2-nitro- (*I*) (○), 3-nitro- (*II*) (●), and 4-nitro- (*III*) (Δ)) acid mixture.

reaction time is shown in Fig. 1. The most pronounced increase of DS was observed between 2 and 3 h, *i.e.* DS \approx 1.3 (*III* and *VII*) and DS \approx 3 (*IV* and *VIII*). In the case of 4-nitrobenzoic acid, the *O*-(4-nitrobenzoyl)cellulose derivatives (*IX—XI*) show a slower increase of DS (0.6–2.0). Further prolongation of the reaction time to 5 h did not affect the DS value (*XII*) significantly.

By lowering the acid/cellulose mole ratio, *e.g.* to 2.22 moles per mole of OH group (*i.e.* 0.0129 mol), new derivative *O*-(4-azidobenzoyl)cellulose (*XIII*) with DS \approx 1 was prepared after reaction at 50°C for 3 h. The lower DS in comparison to the other derivatives was due to the lower reaction ratio and maybe it was influenced by different reactivity of the acid.

Using benzoic acid in the acid/cellulose mole ratio of 3.33:1, the mixed ester *O*-benzoyl-*O*-(methanesulfonyl)cellulose (*XIV*) with DS \approx 0.9 (with regard to the content of the benzoyl groups) was obtained after 3 h reaction time. A higher DS of *O*-benzoylcellulose could not be obtained even at longer reaction time. In contrast to all previously described derivatives, *XIV* exhibited in the IR spectrum the characteristic vibration of the SO_2 group (Table 2) that confirmed binding of the methanesulfonyl (mesyl) groups onto the glucopyranose unit of cellulose. Degree of mesylation (calculated from the content of sulfur) was \approx 0.1. The results reflect the different reactivities of the benzoic acid and its derivatives having electron-attracting substituents ($-\text{NO}_2$, $-\text{N}_3$) in various positions. In the case of the less reactive benzoic acid, the mesylation of cellulose which proceeds only at very low rates under the used experimental conditions [14] could compete with the main esterification reactions.

In the IR spectra (Table 2) of the prepared deriva-

Table 2. IR Spectral Data of the Synthesized Compounds

Compound	$\tilde{\nu}/\text{cm}^{-1}$						
	$\nu(\text{OH})$	$\nu(\text{CH}=\text{C})$	$\nu_{\text{s}}(\text{NO}_2)$	$\nu_{\text{as}}(\text{NO}_2)$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{N}_3)$
<i>I</i>	3344	1442—1608	1354	1537	1743	1255	—
<i>II</i>	3344	1442—1608	1354	1537	1743	1257	—
<i>III</i>	3337	1446—1608	1354	1535	1743	1255	—
<i>IV</i>	3339	1441—1618	1354	1531	1736	1255	—
<i>V</i>	3344	1437—1618	1354	1535	1738	1259	—
<i>VI</i>	3346	1439—1618	1354	1533	1738	1259	—
<i>VII</i>	3343	1441—1618	1354	1533	1740	1259	—
<i>VIII</i>	3339	1441—1618	1354	1531	1736	1255	—
<i>IX</i>	3344	1410—1608	1350	1529	1738	1269	—
<i>X</i>	3343	1412—1608	1350	1529	1738	1267	—
<i>XI</i>	3341	1412—1608	1352	1525	1732	1265	—
<i>XII</i>	3339	1410—1606	1352	1527	1736	1265	—
<i>XIII</i>	3335	1415—1603	—	—	1726	1267	2121
<i>XIV</i>	3335	1423—1603	1174*	1367**	1730	1271	1319***

* $\nu_{\text{s}}(\text{SO}_2)$, ** $\nu_{\text{as}}(\text{SO}_2)$, *** $\delta(\text{CH}_3)$.

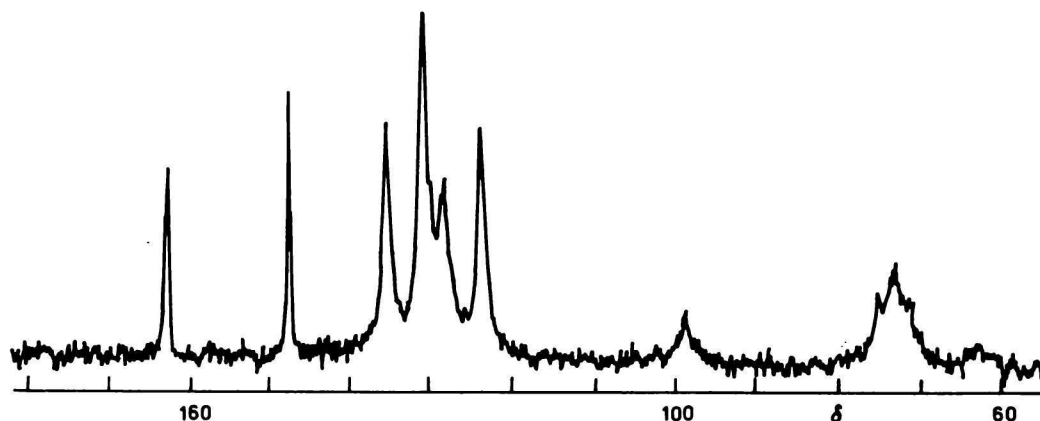


Fig. 2. ^{13}C NMR spectrum of *O*-(3-nitrobenzoyl)cellulose (*VIII*) in $\text{DMSO}-d_6$.

tives, intense absorption bands can be found which correspond in accord with published data [13] to vibrations of the ester groups ($\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$) and benzene ring $\nu(\text{CH}=\text{C})$ bands corresponding to substituents on the benzene ring ($\nu_{\text{s}}(\text{NO}_2)$, $\nu_{\text{as}}(\text{NO}_2)$, and $\nu(\text{N}_3)$). Unlike all other esters prepared from substituted benzoic acids only in the case of the derivative *XIV* the characteristic vibrations of sulfo groups ($\nu_{\text{s}}(\text{SO}_2)$, $\nu_{\text{as}}(\text{SO}_2)$) and the methyl group ($\delta(\text{CH}_3)$) could be found in the IR spectrum.

Because the derivatives were poorly soluble in organic solvents and gave, even at $\text{DS} > 2.0$, gel-like solutions in DMSO, they were subjected to partial hydrolysis to enable the NMR measurements. For illustration, the ^{13}C NMR spectrum of *O*-(3-nitrobenzoyl)cellulose (*VIII*) is shown in Fig. 2. The absence of anomeric carbon signals of reducing end units indicates that the hydrolytic degradation stopped at a low molecular mass polymer. However,

still the carbon signals of the cellulose backbone were broad and poorly resolved. The upfield shift of C-1 to $\delta \approx 98$ and the absence of resonances at $\delta > 80$ and $\delta \approx 60$ indicate, in accord with the α - and β -effects of *O*-acetylation [15], a high degree of esterification. The carbon signals of the main chain were assigned in accord with data published for cellulose esters [14, 16] (Table 3). The spectral patterns of the highly substituted derivatives *IV*, *VII*, and *XII* show marked differences only in the downfield region ($\delta > 100$) where the signals of carbon atoms of the nitrobenzoyl substituents resonate. Due to the higher mobility of the substituents, their signals are dominating in the spectra. They were assigned on the basis of calculations of empirical substituent increments in aromatic compounds [17] (Table 3). Splitting of signals of some substituent carbons indicates their different location and surrounding in the glucose units and thus incomplete substitution of the derivatives.

Table 3. ^{13}C NMR Chemical Shifts^a for Cellulose and Its *O*-(2-Nitrobenzoyl)- (*IV*), *O*-(3-Nitrobenzoyl)- (*VIII*), and *O*-(4-Nitrobenzoyl)- (*XII*) Derivatives

	δ			
	Cellulose ^b	<i>IV</i>	<i>VIII</i>	<i>XII</i>
Glucose ring carbons				
C-1	102.7	98.6	98.3	98.5
C-2	73.2	71.4	71.2	71.4
C-3	74.0	72.8 ^c	72.9 ^c	72.7 ^c
C-4	80.1	75.4	75.0	75.1
C-5	75.1	73.5 ^c	73.4 ^c	73.5 ^c
C-6	60.6	63.5	62.5	62.8
Nitrobenzoyl carbons				
C-1		123.7 (125.2)	130.0 (132.9)	134.4 (135.8)
C-2		148.4 (144.7)	123.2 (122.4)	130.4 (129.1)
C-3		123.7 (123.4)	147.3 (148.2)	123.5 (123.4)
C-4		132.8 (133.1)	146.9 (127.7)	149.5 (132.3)
C-5		133.5 (134.0)	127.7 (129.1)	123.0 (123.4)
C-6		129.8 (129.1)	129.8 (134.0)	129.9 (127.3)
C-7		130.1 (162.7)	162.6 (162.8)	162.8 (163.7)

a) In DMSO- d_6 ; b) Ref. [18]; c) may be interchanged. Values in brackets are calculated according to Ref. [17].

Finally, it can be concluded that the new preparation method of cellulose esters with substituted benzoic acids in the system pyridine—methanesulfonyl chloride—acid represents a suitable way of synthesis of highly substituted derivatives. Both the relatively short reaction time (2–3 h) and the low temperature ($\approx 50^\circ\text{C}$) of the reaction represent the most pronounced advantages of the method described above.

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