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SYNTHESIS AND PROPERTIES OF CELLULOSE FUROATES. NUCLEOPHILIC DISPLACEMENT REACTIONS OF BROMO-SUBSTITUTED CELLULOSE FUROATES WITH TERTIARY AMINES*

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ABSTRACT

Cellulose furoates were prepared by the reaction of purified cotton cellulose with 2-furoyl chloride, 5-bromo-2-furoyl chloride, 5-methyl-2-furoyl chloride, and 2-furanacryloyl chloride in pyridine as the acid scavenger, with *N,N*-dimethylformamide as the diluent. The bromo-substituted cellulose furoates underwent nucleophilic displacement reactions with pyridine, *N,N*-dimethylcyclohexylamine, and triethylamine to give the corresponding quaternary salts. Infared spectra and physical properties of the fibrous cellulose furoates are reported. The mechanism of the nucleophilic displacement reaction is discussed.

INTRODUCTION

The properties of cotton cellulose have been modified by the preparation of chemical derivatives and graft copolymers of cellulose. For example, the reaction of 2-furoyl chloride with cellulose in the presence of pyridine was reported by Chatterjee and Stanonis[1] and Shaposhnikova *et al.*[2]. In the former article, no details were given regarding the identification or properties of the products. When the reactions were conducted in chloroform, dichloromethane, tetrachloroethane[3], and ethyl acetate, highly colored yarns were obtained. In dry *N,N*-dimethylformamide (DMF), the yarns obtained were less colored. The temperature during all of these reactions was 78–80°, at which, less colored yarns were obtained than at higher temperatures. Polyakov and Rogovin[4] found that, when cellulose was treated with thionyl chloride in dry DMF at 80° (without pyridine), reaction occurred and the hydrogen chloride evolved complexed with DMF. We have found that no reaction occurs when cellulose is treated with furan acid chlorides in dry DMF at 80°, unless pyridine is added. However, at 100–110°, reaction occurs without pyridine, and hydrogen chloride is evolved; at the end of the reaction, the treated yarns were found to be highly degraded by the acid.

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RESULTS AND DISCUSSION

The preparation of cellulose furoates is described in this report. In an attempt to prepare cotton cellulose yarns having modified physical properties, yarns were treated with 2-furoyl chloride, 5-methyl-2-furoyl chloride, 5-bromo-2-furoyl chloride, and 2-furanacryloyl chloride in pyridine as the acid scavenger, with dry DMF as the diluent.

The conditions for reaction of 2-furoyl chloride with purified cotton cellulose and the properties of the products are given in Table I. The degree of substitution (D. S.) of the products was dependent on the concentrations of the reactants and the reaction time. The i.r. spectrum of purified cotton cellulose is shown in Fig. 1A, and that of a product (D. S. 1.26), in Fig. 1B. The differential i.r. spectrum, obtained by instrumentally subtracting spectrum 1A from spectrum 1B, is shown in Fig. 1C; λ_{max}^{KBr} 5.80 (ester) and 6.35 μm (aromatic).

TABLE I

CONDITIONS FOR FORMATION, AND PROPERTIES, OF CELLULOSE FUROATES

Molar proportions of reactants[a]	*Reaction time, h*	*Degree of substitution*	*Breaking strength* $\times 10^{-3}$ (g)	*Color of product*
2-Furoyl chloride[b]				
(control)	—	0.00	4.77	white
1:4·8	6	1.26	4.84	very light-yellow
1:5:10	7	1.72	3.96	yellow
1:4.8	11	1.86	3 22	yellow
1:8:16	12	2.73	0.92	deep-yellow
5-Methyl-2-furoyl chloride[b]				
(control)	—	0.00	4.77	white
10.33:66	9	1.22	3.34	light-yellow
1:5:10	9	1.45	3.09	yellow
2-Furanacryloyl chloride[b]				
(control)	—	0.00	4.77	white
5:12·24	10	1.01	4.94	deep-yellow
5:38:76	10	1.89	1.44	brown-yellow
5-Bromo-2-furoyl chloride				
(control[b])	—	0.00	2 43	white
1:5:10[b]	6	79[c]	1.10	brown-black
1:4.8[b]	20	190[c]	0.64	black
1:4:8[d]	6	9.6[c]	1.59	white-yellow
1:4·8[e]	15	9.5[c]	1.71	yellow

[a] Molar ratios of D-glucose residue acid chloride·base; reaction temperature, 78–80°; DMF diluent. [b] Pyridine used. [c] Add-on, % [d] *N*,*N*-Dimethylcyclohexylamine used. [e] Triethylamine used.

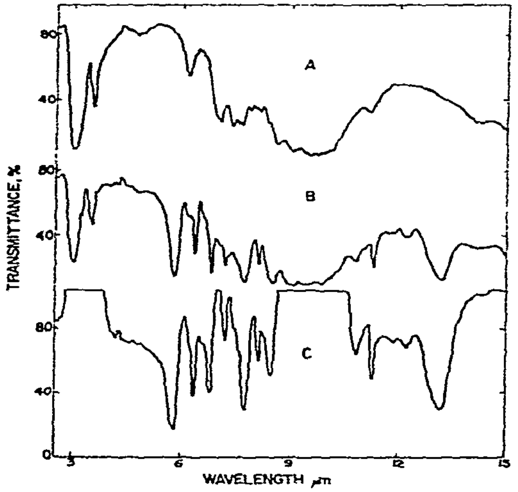


Fig 1. Infrared spectra of cotton cellulose (A) and of cotton cellulose treated with 2-furoyl chloride (B, product; C, differential spectrum).

The conditions for reaction of 5-methyl-2-furoyl chloride with cellulose, and the properties of the products, are given in Table I. The i.r. spectrum of a product (D. S. 1.45) is shown in Fig. 2A, and the differential i.r. spectrum in Fig. 2B; λ_{max}^{KBr} 5.80 (ester) and 6.28 μm (aromatic).

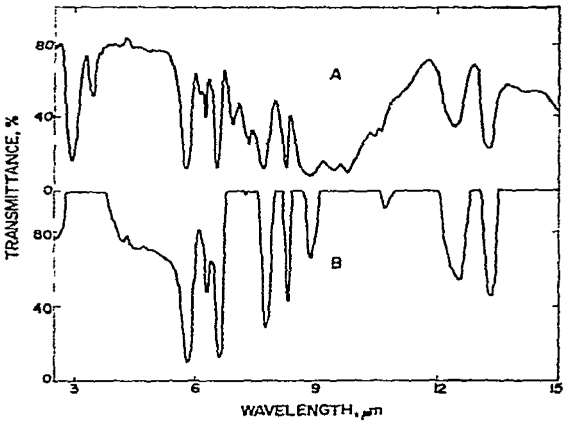


Fig. 2. Infrared spectrum of cotton cellulose treated with 5-methyl-2-furoyl chloride (A, product; B, differential spectrum)

The conditions for reaction of 2-furanacryloyl chloride with cellulose and the properties of the products are given in Table I. The i.r. spectrum of a product (D. S. 1.89) is shown in Fig. 3A, and the differential i.r. spectrum, in Fig. 3B; λ_{max}^{KBr} 5.81 (ester), 6.10 (C = C), and 6.41 μm (aromatic).

In dry DMF, the complex formed on reaction of pyridine with 2-furanacryloyl chloride was less soluble than the complexes formed on reaction with 2-furoyl chloride or 5-methyl-2-furoyl chloride. Consequently, for the first complex, a larger proportion of dry DMF was needed in order to give a homogeneous solution than for the last two.

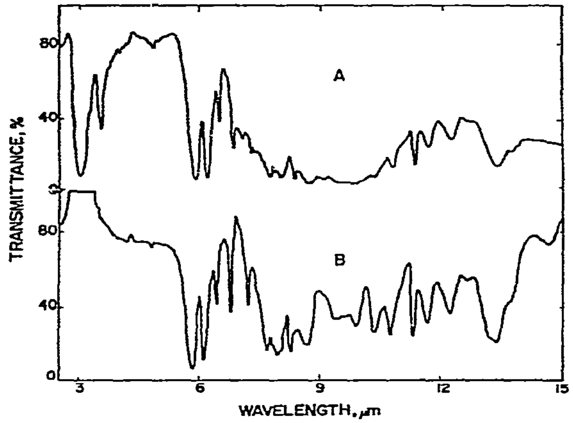
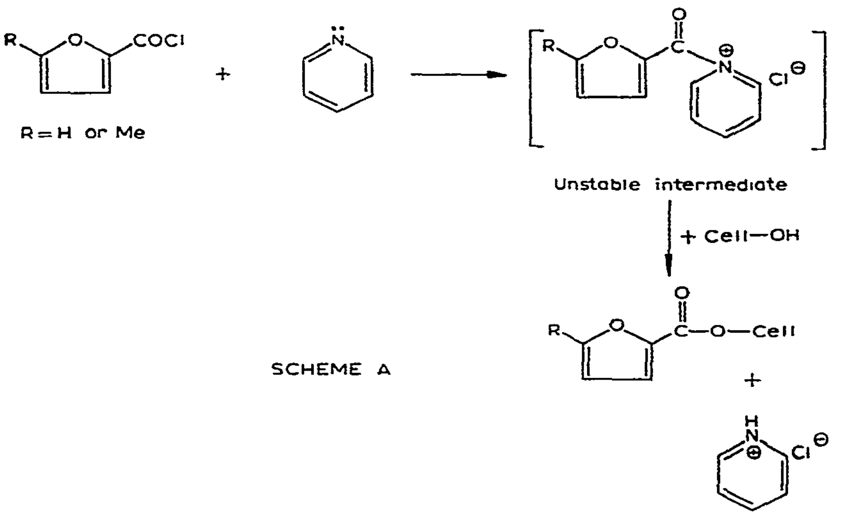


Fig. 3. Infrared spectrum of cotton cellulose treated with 2-furanacryloyl chloride (A, product; B, differential spectrum).

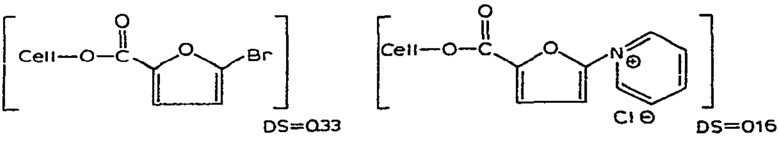
The i.r. spectra indicated that furoylation of cellulose occurred; a possible scheme is given in Scheme *A*. The ease[5] with which cinnamoyl chloride reacts with pyridine to give cinnamoylpyridinium chloride supports this Scheme.



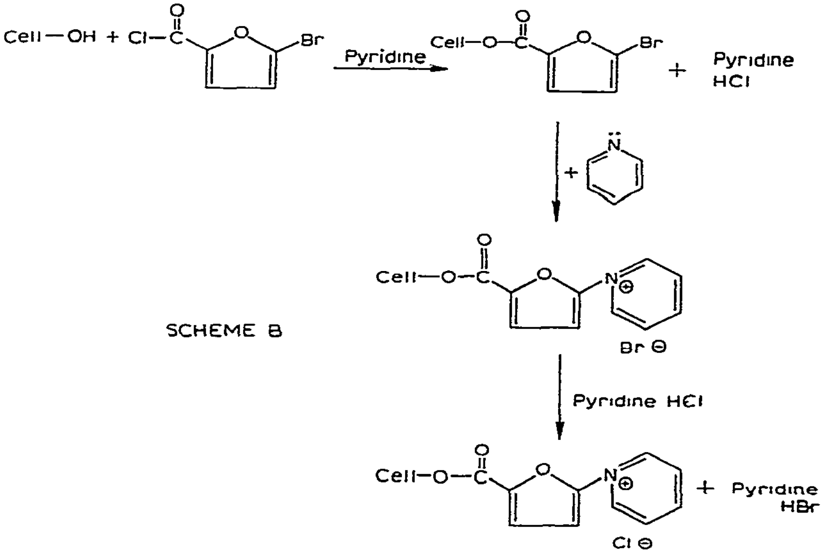
SCHEME A

The nucleophilic displacement reactions of vinyl halides have been described from both the mechanistic and the synthetic point of view[6,7]. The vinyl halides are usually unreactive in nucleophilic substitution reactions; they are reactive with such strong, electron-withdrawing groups as COR, COOR, SOR, SOOR, and CN, which, by inductive or mesomeric effects, or both, facilitate nucleophilic attack by the reagent at the carbon atom bonded to the halogen atom[8–13]. The rates of reaction of halides of aliphatic and aromatic compounds with such nucleophilic reagents as hydroxides, alkoxides, ammonia, and amines have been reported[14]. Kinetic studies have been reported of the reaction of 2-bromofuran with piperidine at 199° in a sealed tube[15]. We have found[16] that, when 2-bromofuran is activated by electron-withdrawing groups, a nucleophilic displacement reaction with piperidine occurs at 80°. A prime reason for the present work was to compare the extent of reaction of halogen-substituted heterocyclic systems having electron-withdrawing groups with that of vinyl halides similarly substituted.

The conditions of reaction of 5-bromo-2-furoyl chloride with cellulose in pyridine, and the properties of the products, are given in Table I. The product obtained after reaction for 6 h had 79.4% "add-on" (increase in weight), and contained Br 10.09, Cl 2.15, N 0.81, and H_2O 3.10%. This composition corresponds to a mixed derivative of cellulose, as in I. A possible reaction scheme is shown in Scheme *B*. The i.r. spectrum of the product is shown in Fig. 4A, and the differential i.r. spectrum, in Fig. 4B; λ_{max}^{KBr} 3.35 (aromatic CH, pyridine), 6.14, 6.25 (aromatic), and 5.80 μm (ester). These data further confirm that formation of the quaternary salt had occurred.



(I)



SCHEME B

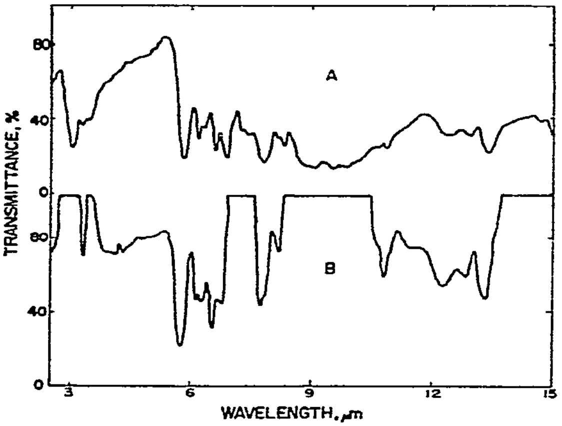
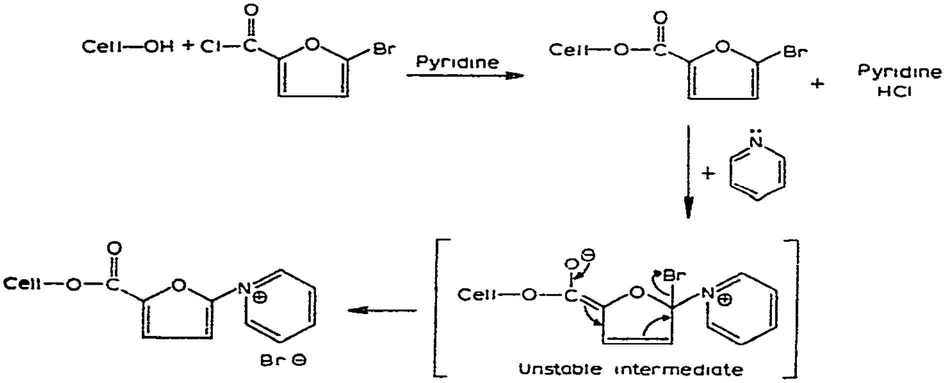


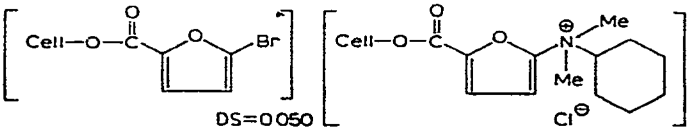
Fig. 4. Infrared spectrum of cotton cellulose treated with 5-bromo-2-furoyl chloride in pyridine (A, product; B, differential spectrum)

The most likely mechanism for the reaction of 5-bromo-2-furoyl chloride with cellulose in pyridine involves conjugate addition–elimination, as shown in Scheme *C*.



SCHEME C

Nucleophilic reactivity generally depends on the strength of the base used. Piperidine, a stronger base than pyridine, reacted with the acid chloride, and a quantitative yield of 5-bromo-*N*,*N*-pentamethylene-2-furoamide was obtained. In *N*,*N*-dimethylcyclohexylamine, a cellulosic product having 9.64% "add-on" was obtained; it contained Br 2.18, Cl 0.79, N 0.084, and H_2O 3.05%. This composition could correspond to a mixed derivative of cellulose, as in II.



(II)

Brady and Cropper[17] reported that amines having a number of alkyl groups attached to, or near, their nitrogen atoms are, in general, less reactive than amines having less branching near the nucleophilic center. They observed that, in some structures, alkyl groups interfere with the approach of the nitrogen atom to the aromatic carbon atom, whereas alkyl groups do not affect the basicity of the amine. Their argument, namely, that the intrinsic nucleophilic activity of the amines is modified by the steric effects of the alkyl groups, is convincing; it is applicable to *N*,*N*-dimethylcyclohexylamine and triethylamine. Cellulosic yarns treated with 5-bromo-2-furoyl chloride in *N*,*N*-dimethylcyclohexylamine and triethylamine are slightly yellow. When the reaction is conducted in pyridine, the yarns are dark-brown. The properties of the products obtained on reaction of 5-bromo-2-furoyl chloride with cellulose in *N*,*N*-dimethylcyclohexylamine are shown in Table I. The i.r. spectrum of the product is shown in Fig. 5A, and the differential i.r. spectrum, in Fig. 5B; λ_{max}^{KBr} 5.81 (ester) and 6.35 μm (aromatic).

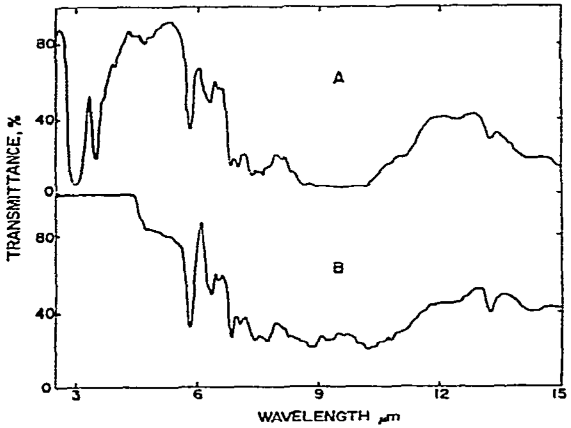
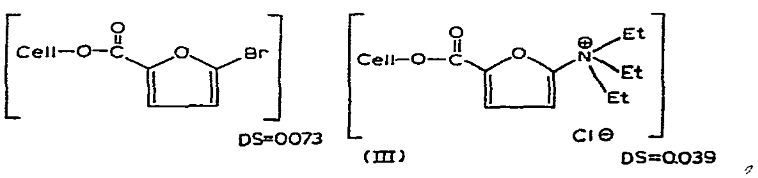


Fig. 5. Infrared spectrum of cotton cellulose treated with 5-bromo-2-furoyl chloride in *N*,*N*-dimethylcyclohexylamine (A, product; B, differential spectrum).

In triethylamine, a cellulosic product having 9.51% "add-on" was obtained; it contained Br 2.93, Cl 0.71, N 0.33, and H_2O 5.84%. This composition corresponds to a mixed derivative (III) of cellulose. The i.r. spectrum of the product is shown in



(III)

Fig. 6A, and the differential i.r. spectrum, in Fig. 6B; λ_{max}^{KBr} 5.82 (ester) and 6.35 μm (aromatic). The reaction conditions, and the properties of the products, are given in Table I.

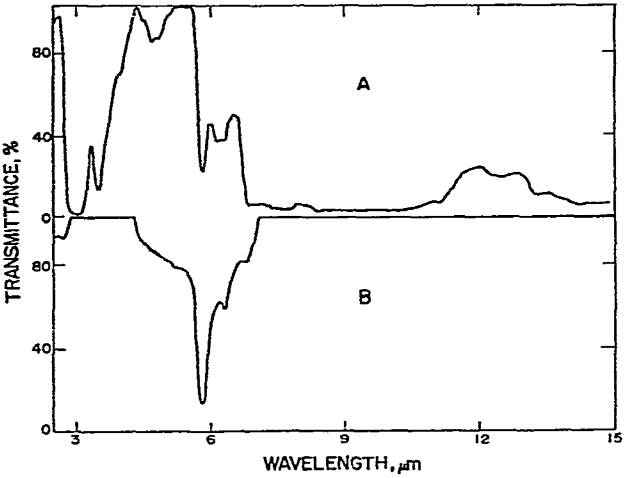


Fig. 6. Infrared spectrum of cotton cellulose treated with 5-bromo-2-furoyl chloride in triethylamine (A, product; B, differential spectrum).

EXPERIMENTAL

Materials. — Pyridine was dried over solid potassium hydroxide for 24 h, and distilled. *N,N*-Dimethylformamide (analytical grade) was dried over Drierite*, and purified by distillation. 2-Furoyl chloride was obtained from Eastman Kodak Co.; it was purified by distillation, b.p. 64–65°/10 torr.

5-Bromo-2-furoyl chloride was prepared by boiling a solution of 5-bromo-2-furoic acid (m.p. 186–187°; 1 mole) (prepared by the method of Whittaker[18]) and thionyl chloride (1.5 moles) in dry benzene for 20 h under reflux, and evaporating to dryness in a flash evaporator. The residue was vacuum-distilled, and a fraction of b.p. 78–81°/25 torr was collected; it solidified completely within 0.5 h; yield 90%, m.p. 59–60°; lit.[19] m.p. 58–60°.

5-Methyl-2-furoyl chloride was prepared by the method of Mudzhoyan *et al.*[20] by boiling 5-methyl-2-furoic acid (1 mole) and thionyl chloride (1.5 moles) in dry benzene under reflux, it was a colorless liquid, b.p. 136–138°/66 torr, yield 92%, that solidified completely on standing.

2-Furanacryloyl chloride was prepared by boiling a solution of 2-furanacrylic acid (*trans* acid, m.p. 141°; 1 mole) and thionyl chloride (1.5 moles) in dry benzene for 20 h under a reflux condenser (calcium chloride tube). The solution was evaporated to dryness under diminished pressure (25 torr), and the residue was distilled at 75–80°/0.45 torr; lit.[21] b.p. 90°/2 torr. The distillate, obtained in 90% yield, solidified on standing.

Deltapine cotton in the form of 7s/3 yarn was purified by the method of Arthur and Mares[22] to yield cellulose (mol. wt. 700,000).

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*Trade names are given as part of the exact experimental conditions, and not as an endorsement of the products over those of other manufacturers.

Methods. — The reactions were conducted by placing weighed yarn in an all-glass, tube apparatus described by Hamalainen *et al.*[23]. Physical tests were performed by ASTM methods[24]. I.r. spectra of potassium bromide discs were recorded with a Perkin–Elmer double-beam spectrophotometer. Differential i.r. techniques were used for identifying the products. Elemental analyses were made by Galbraith Laboratories, Knoxville, Tennessee. The degree and uniformity of the esterification was determined by a dye test that uses mixed Acetate Yellow and Direct Cotton Blue[25]; the test was performed only for light-colored products.

Reaction conditions. — Dry DMF (100 to 300 ml, depending on the acid chloride used) was placed in the glass-tube apparatus[23], the desired amount of acid chloride (freshly distilled) was added, and dry pyridine (freshly distilled; 2 moles per mole of acid chloride) was added dropwise during 15 min. The mixture was then shaken by repeatedly inverting the tube; a colorless solution resulted. (A colored solution was formed if the acid chloride and pyridine were not freshly distilled.) Cellulose (~4–8g), in the form of yarn predried at 60° for 2 h, was added to the solution, and the tube was placed in an oil bath at 78–80°. The contents of the tube were shaken every 30 min. After completion of the reaction, the yarns were removed from the solution, washed twice with DMF, and immersed[26] in warm methanol (50–60°). The yarns were then kept in 10% potassium hydrogen carbonate solution for 0.5 h, and washed thoroughly with distilled water. Before being weighed or tested, all of the yarns were equilibrated for 24 h at about 50% relative humidity at 25°. The extent of reaction was ascertained by determining the increase in weight ("add-on") of these samples over that of the control yarn. Yarns esterified to various degrees of substitution (D.S.) with each acid were obtained by altering the ratio of molar concentration of acid chloride to cellulose, or the reaction time, or both.

A reaction did not occur between cellulose and 5-bromo-2-furoyl chloride when, instead of pyridine or *N,N*-dimethylcyclohexylamine, piperidine was used as the acid scavenger; 5-bromo-*N,N*-pentamethylene-2-furoamide was obtained in 89% yield. The crude amide was recrystallized twice from hexane (decolorizing carbon); m.p. 66–67°; $\lambda_{max}^{CHCl_3}$ 6.20 and 6.40 μm; n.m.r. data ($CDCl_3$): τ 3.10 (doublet, H-1), 3.60 (doublet, H-1), 6.30 (multiplet, H-4), and 8.35 (multiplet, H-6).

Anal. Calc. for $C_{10}H_{12}BrNO_2$: C, 46.51; H, 4.65; Br, 31.00; N, 5.42. Found: C, 46.32; H, 4.86; Br, 30.90; N, 5.52.

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