SYNTHESIS AND PROPERTIES OF CELLULOSE 2-THENOATES. NUCLEOPHILIC DISPLACEMENT REACTIONS OF BROMO-SUBSTITUTED 2-THENOATES OF CELLULOSE WITH TERTIARY AMINES*

SUJAN SINGH** AND JETT C. ARTHUR, JR.

Southern Regional Research Laboratory, Southern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture, New Orleans, Louisiana 70119 (U. S. A.)

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ABSTRACT

The 2-thenoate*** and some substituted 2-thenoates of cellulose were prepared by the reaction of purified cotton cellulose with 2-thenoyl chloride (**1**), 5-methyl-2-thenoyl chloride (**2**), 2-thiopheneacryloyl chloride (**3**), 5-bromo-2-thenoyl chloride (**4**), and 5-bromo-2-thiopheneacryloyl chloride (**5**), in pyridine as the acid scavenger, with *N,N*-dimethylformamide as diluent. The bromo-substituted 2-thenoates of cellulose, obtained by reaction with **4** and **5**, respectively, undergo nucleophilic displacement reactions with pyridine, *N,N*-dimethylcyclohexylamine, and triethylamine to give the corresponding quaternary salts; the mechanism of the nucleophilic displacement reaction is discussed. The infrared spectra and other physical properties of the fibrous 2-thenoate and substituted 2-thenoates of cellulose are reported.

INTRODUCTION

We have recently reported on the synthesis and properties of cellulose furoates[1], an electron spin resonance study of intramolecular energy-transfer during the radiolysis of cellulose furoates[2], and the rot-resistance properties of fibrous cellulose furoates[3]. These investigations have now been extended to the synthesis and properties of heterocyclic derivatives of cellulose by synthesizing substituted 2-thenoates of cellulose.

RESULTS AND DISCUSSION

Purified, fibrous cotton-cellulose was esterified, usually in the yarn form, with 2-thenoyl chloride (**1**), 5-methyl-2-thenoyl chloride (**2**), 2-thiopheneacryloyl chloride (**3**), 5-bromo-2-thenoyl chloride (**4**), and 5-bromo-2-thiopheneacryloyl chloride (**5**)

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**NRC Resident Postdoctoral Research Associate, 1968–1970.
***2-Thenoic acid is a convenient abbreviation for 2-thiophenecarboxylic acid.

in the presence of pyridine as the acid scavenger and dry *N,N*-dimethylformamide (DMF) as the diluent. During all of these reactions, the temperature was kept at 80–85°, because less-colored products were thus obtained than at higher temperatures. Highly colored products were obtained when the reactions were conducted in chloroform, dichloromethane, tetrachloroethane, and ethyl acetate. No reaction occurs when cellulose is treated with these 2-thiophenecarboxylic acid chlorides in *p*-dioxane as the diluent; the complexes formed by combination of the acid chlorides with pyridine are insoluble in *p*-dioxane at 80–85°.

The conditions for reaction of chlorides **1**, **2**, and **3** with purified cotton-cellulose yarns and the properties of the products are given in Table I. In all of these reactions,

TABLE I

CONDITIONS FOR FORMATION, AND PROPERTIES, OF CELLULOSE 2-THENOATES

Molar proportions of reactants[a]	*Reaction time, h*	*Degree of substitution (D.S.)*	*Breaking strength* $\times 10^{-3}$, *g*	*Color of product*
2-Thenoyl chloride				
(control)	—	0.00	4.73	white
1:2:4	6	0.15	4.24	white
1:2:4	24	0.21	3.86	white
1:4:8	20	0.36	3.96	white–yellow
1:4:8	24	0.46	2.55	light-yellow
1:6:12	36	0.96	2.29	yellow
5-Methyl-2-thenoyl chloride				
(control)	—	0.00	4.57	white
1:2:4	12	0.25	1.57[b]	light-yellow
1:4:8	24	0.56	3.45	light-yellow
2-Thiopheneacryloyl chloride				
(control)	—	0.00	4.71	white
1:1:2	40	0.06	2.21	light-yellow
1:3:6	24	1.43	4.38	yellow

[a]Molar ratios of D-glucose residue:acid chloride:pyridine; reaction temperature, 80–85°; DMF diluent; dried under stretched conditions. [b]Dried under slack conditions.

the complexes formed on reaction of the acid chlorides with pyridine, triethylamine, or *N,N*-dimethylcyclohexylamine were soluble in dry DMF at 80–85°. The degree of substitution (D. S.) of the products was dependent on the concentration of the reactants and the reaction time. The i.r. spectrum of purified cotton cellulose is shown in Fig. 1 (1A), and that of a product (D. S. 0.96) from reaction with **1**, in Fig. 1 (1B); λ_{max}^{KBr} 5.80 (ester) and 6.25 μm (aromatic). The i.r. spectrum of a product (D. S. 0.25) from reaction with **2** is shown in Fig. 1 (2A). The differential i.r. spectrum, obtained by instrumentally subtracting spectrum 1A from spectrum 2A, is shown in Fig. 1 (2B); λ_{max}^{KBr} 3.10 (aromatic, CH) and 5.88 μm (ester). The i.r. spectrum of a product (D. S. 1.43) from reaction with **3** is shown in Fig. 1 (3A). The differential i.r. spectrum, obtained by instrumentally subtracting spectrum 1A from spectrum 3A, is shown in Fig. 1 (3B); λ_{max}^{KBr} 5.85 (ester) and 6.25 μm (C=C, aromatic).

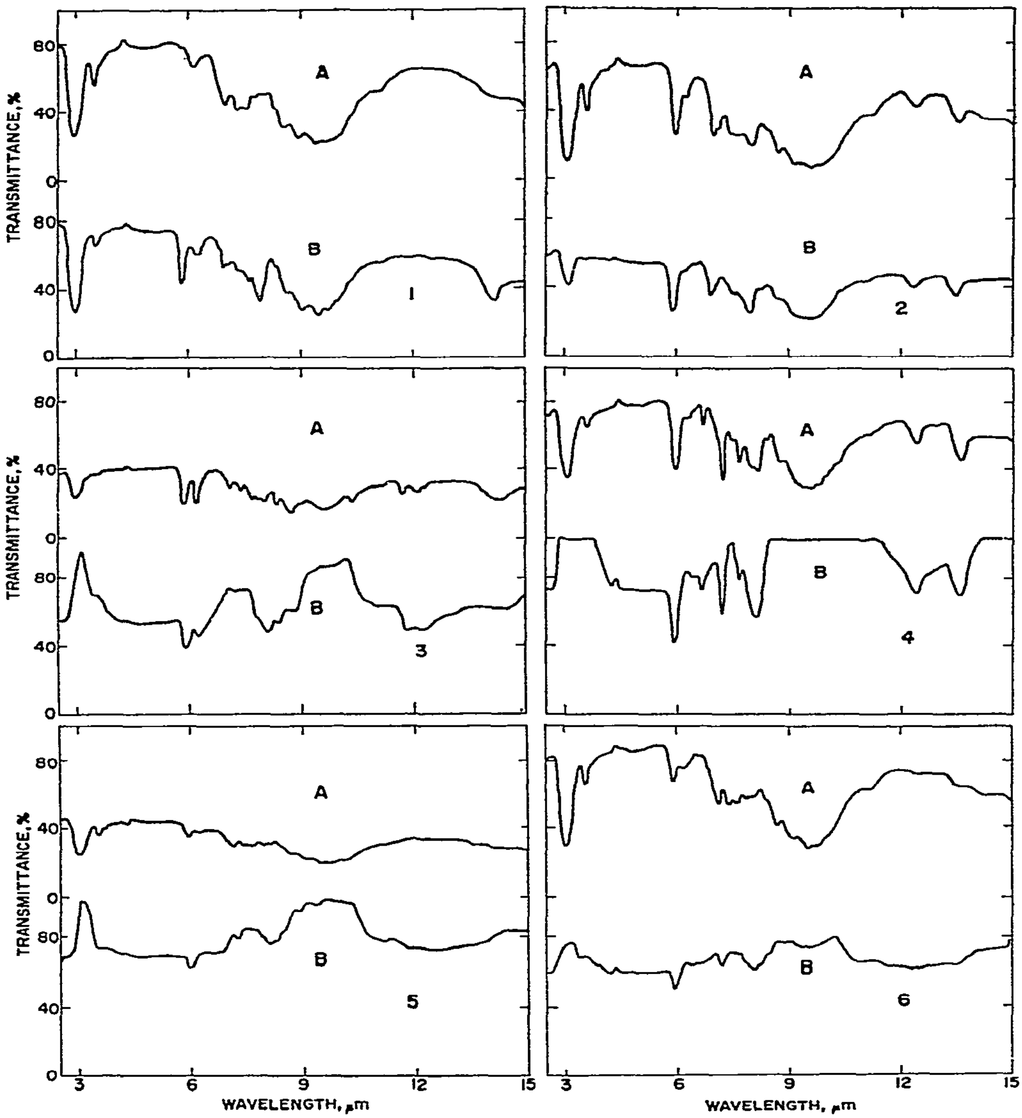
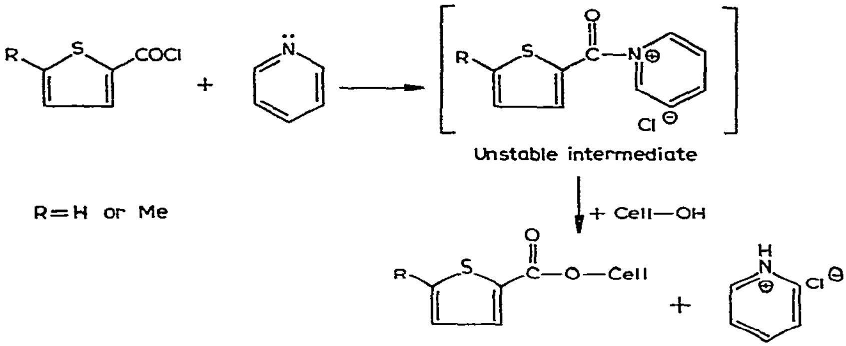


Fig. 1. Infrared spectra: 1, cotton cellulose (A) and cotton cellulose treated with **1** (B); 2, cotton cellulose treated with **2**; 3, treated with **3**; treated with **4** (4, in pyridine; 5, in triethylamine; and 6, in *N,N*-dimethylcyclohexylamine; A, product; B, differential spectrum).

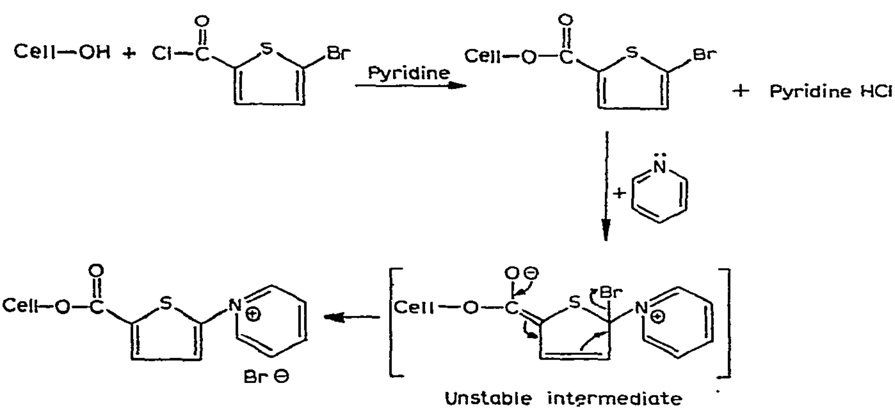
The i.r. spectra and the results of the dye tests indicated that thenoylation of cellulose had occurred; a possible scheme is given in Scheme A. A similar scheme has been proposed for the furoylation of cellulose[1]. This scheme is also supported by the ease with which cinnamoyl chloride reacts with pyridine to give cinnamoylpyridinium chloride[4].

When purified cotton cellulose was treated with 5-bromo-2-thenoyl chloride (4) or 5-bromo-2-thiopheneacryloyl chloride (5) in the presence of pyridine, triethylamine, or *N,N*-dimethylcyclohexylamine, the resulting bromo-substituted 2-thenoates of cellulose underwent nucleophilic displacement reactions with these tertiary amines



SCHEME A

to give the corresponding quaternary salts. The products contained chlorine, as well as bromine, nitrogen, and sulfur. In contrast, 2-bromothiophene does not undergo such a reaction with piperidine or pyridine in dry DMF at 80–85°. A possible scheme for the reaction of 4 or 5 with cellulose in pyridine involves conjugate addition–elimination, as shown in Scheme B. Reaction of the initial product with pyridinium chloride, shown in Scheme B, in which the bromine of the initial product is partially



SCHEME B

displaced by chlorine, would explain these results. Similarly, vinyl halides, usually unreactive in nucleophilic reactions, become reactive on substitution with strong electron-withdrawing groups[5–12]. Bromo derivatives of vinyl halides also undergo elimination reactions more readily than chloro derivatives[13].

The conditions of reaction of **4** with cellulose in pyridine, and the properties of the products, are given in Table II. The products obtained after reaction for 24 h

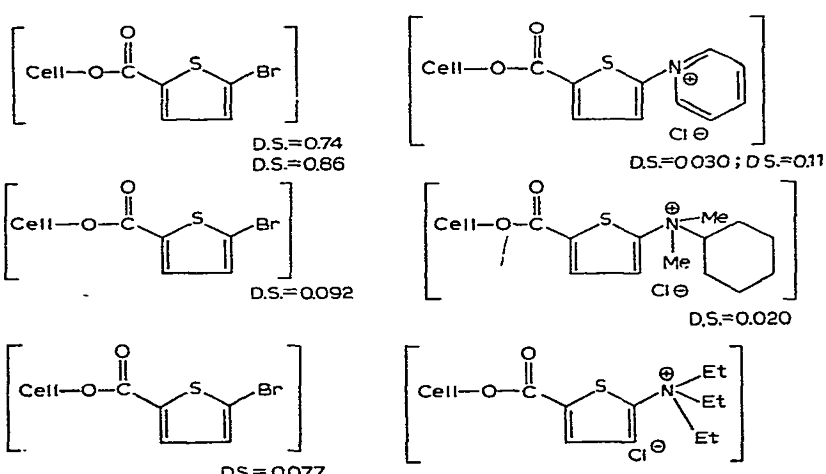
TABLE II

CONDITIONS FOR FORMATION, AND PROPERTIES, OF BROMO-SUBSTITUTED 2-THENOATES OF CELLULOSE

Molar proportions of reactants[a]	*Reaction time, h*	*"Add-on", %*	*Nitrogen, %*	*Breaking strength* $\times 10^{-3}$, *g*	*Color of product*
5-Bromo-2-thenoyl chloride					
(control)	—	0.0	—	4.63	white
1:4:8[b]	24	80	0.13	4.78	light-yellow
1:4:8[b]	60	99	0.45	1.71	dark-brown
1:4:8[c]	48	10	0.13	1.55	light-yellow
1:4:8[d]	48	12	0.14	2.19	light-yellow
5-Bromo-2-thiopheneacryloyl chloride					
(control)	—	0.0	—	4.73	white
1:4:8[b]	24	250	0.13	2.26	yellow
1:4:8[b]	60	268	0.27	2.20	dark-brown
1:3:8[c]	28	8.1	0.05	3.72	light-yellow
1:3:8[d]	40	11	0.06	3.33	light-yellow

[a]Molar ratios of D-glucose residue:acid chloride:base; reaction temperature, 80–85°; DMF diluent. [b]Pyridine used. [c]Triethylamine used. [d]*N*,*N*-Dimethylcyclohexylamine used.

had 80% "add-on" (increase in weight), and contained Br 18.36, Cl 0.33, N 0.13, S 7.62, and H_2O 2.39%. The products obtained after reaction for 60 h had 99% "add-on", and contained Br 19.40, Cl 1.15, N 0.45, S 9.39, and H_2O 2.29%. The compositions of these products correspond to the mixed derivatives of cellulose, as



(I)

given in I. The i.r. spectrum of the product with 80% "add-on" is shown in Fig. 1 (4A), and differential i.r. spectrum, in Fig. 1 (4B); λ_{max}^{KBr} 3.40, 5.80, 6.35, and 6.60 μm.

The conditions of reaction of **4** with cellulose in triethylamine and in *N*,*N*-dimethylcyclohexylamine, and the properties of the products, are also given in Table II. The products obtained after reaction for 48 h had 10 and 12% "add-on", respectively, and contained Br 3.85, Cl 0.33, N 0.13, S 1.58, and H_2O 4.97% (triethylamine) and Br 3.66, Cl 0.35, N 0.14, S 1.47, and H_2O 4.59% (*N*,*N*-dimethylcyclohexylamine). The compositions of these products correspond to the mixed derivatives of cellulose, as in I. The i.r. spectrum of the first product is shown in Fig. 1 (5A), and the differential i.r. spectrum, in Fig. 1 (5B); λ_{max}^{KBr} 5.85 μm. The i.r. spectrum of the second product is shown in Fig. 1 (6A), and the differential i.r. spectrum, in Fig. 1 (6B); λ_{max}^{KBr} 5.90 μm.

The conditions of reaction of chloride **5** with cellulose in pyridine, and the properties of the products, are given in Table II. The products obtained after reaction for 24 h had 250% "add-on", and contained Br 25.59, Cl 0.33, N 0.13, S 7.62, and H_2O 1.41%. The products obtained after reaction for 60 h had 268% "add-on", and

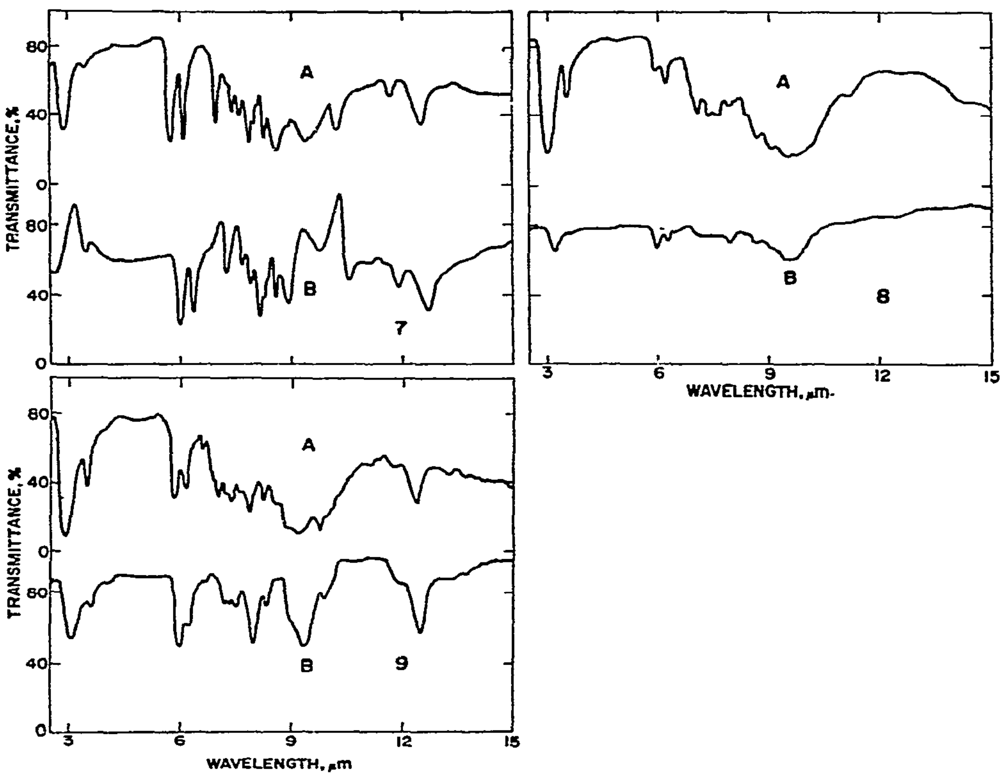
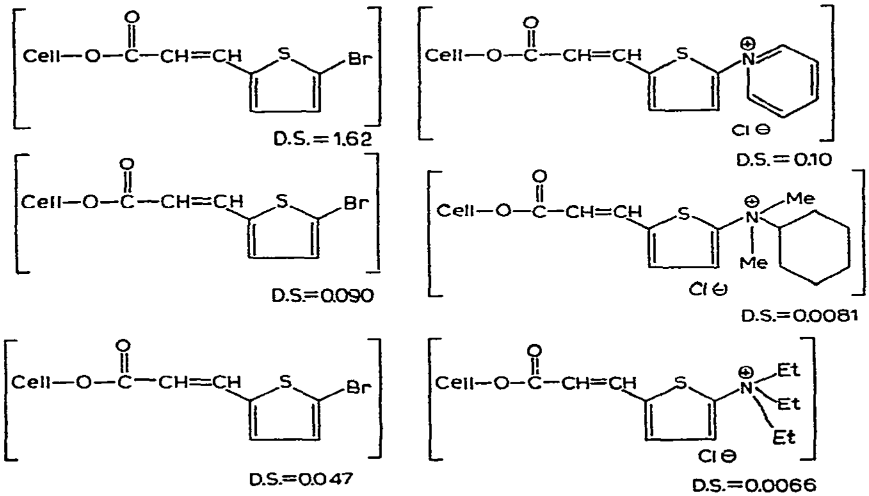


Fig. 1 (contd.). Infrared spectra of cotton cellulose treated with 5 (7, in pyridine; 8, in triethylamine; 9, in *N*,*N*-dimethylcyclohexylamine; A, product; B, differential spectrum).

contained N 0.27%. The i.r. spectrum of the product with 250% "add-on" is shown in Fig. 1 (7A), and the differential i.r. spectrum, in Fig. 1 (7B); λ_{max}^{KBr} 3.45, 6.30, and

5.95 μm. The composition of the product corresponds to that calculated for a mixed derivative of cellulose, as in II.



(II)

The conditions of reaction of chloride **5** with cellulose in triethylamine and in *N*,*N*-dimethylcyclohexylamine, and the properties of the products, are given in Table II. The product obtained after reaction for 28 h in triethylamine had 8.1% "add-on", and contained Br 2.13, Cl 0.71, N 0.05, S 0.78, and H_2O 3.88%. The product obtained after reaction for 40 h in *N*,*N*-dimethylcyclohexylamine had 11% "add-on", and contained Br 3.76, Cl 0.58, N 0.06, S 1.47, and H_2O 3.53%. The i.r. spectrum of the first product is shown in Fig. 1 (8A), and the differential i.r. spectrum, in Fig. 1 (8B); λ_{max}^{KBr} 3.25, 5.95, and 6.25 μm. The i.r. spectrum of the second product is shown in Fig. 1 (9A), and the differential i.r. spectrum, in Fig. 1 (9B); λ_{max}^{KBr} 3.05, 3.55, 5.95, and 6.25 μm. The compositions of the products correspond to the mixed derivatives of cellulose, as in II.

Piperidine, a stronger base than pyridine, reacts with both **4** and **5**; quantitative yields of 5-bromo-*N*,*N*-pentamethylene-2-thienamide and 5-bromo-*N*,*N*-pentamethylene-2-thiopheneacrylamide, respectively, were obtained. The identities of the products were confirmed by i.r. spectroscopy and elemental analysis. The n.m.r. spectra of the two amides did not, however, show the expected characteristic quartet of lines of the AB pattern of two protons on the thiophene ring, and only a singlet appeared. Apparently, the electronic effects of the bromo substituent and the amide linkage cause the protons on the thiophene ring to experience identical magnetic fields; the protons thus became equivalent under the conditions of resolution used. The extent of reaction of the acid chlorides with cellulose in triethylamine or in *N*,*N*-dimethylcyclohexylamine was less than that in pyridine; this may indicate steric effects[1,14] of alkyl groups on the nitrogen atom to yield weaker nucleophiles than for pyridine.

EXPERIMENTAL

Materials. — Pyridine, piperidine, triethylamine, and *N,N*-dimethylcyclohexylamine were dried with solid potassium hydroxide for 48 h, and distilled. *N,N*-Dimethylformamide (analytical grade) was purified by distillation from calcium hydride.

2-Thenoyl chloride (**1**) was prepared by boiling a suspension of 2-thiophenecarboxylic acid (1 mole) and thionyl chloride (1.3 moles) in dry benzene under reflux for 8 to 10 h. As hydrogen chloride was liberated, the suspended material dissolved. The solvent and the excess of thionyl chloride were evaporated in a flash evaporator, the residue was distilled under vacuum, and a fraction of b.p. 144–146°/30 torr was collected; yield 95%; lit.[15] b.p. 77°/10 torr. It showed λ_{max}^{film} 5.75 and 6.70 μm.

5-Bromo-2-thiophenecarboxylic acid was synthesized by the oxidation of 5-bromo-2-thenaldehyde, prepared by the method of Buu-Hoi and Lavit[16]. A mixture of 5-bromo-2-thenaldehyde (0.1 mole) and 500 ml of water was heated on a steam bath to give an emulsion; then a solution of potassium permanganate (0.15 mole) in distilled water (1.5 liters) was added dropwise during 1 h. After the solution had been heated for 2 h, it was made alkaline with potassium hydroxide; the hot mixture was filtered, and the resulting manganese dioxide was washed with three 250-ml portions of hot water. Acidification of the filtrate gave a solid product which, on recrystallization from dilute ethanol, gave 18.63 g (90% yield) of pure 5-bromo-2-thiophenecarboxylic acid, m.p. 142–143°; lit.[17,18] m.p. 141–142°.

5-Bromo-2-thenoyl chloride (**4**) was prepared by boiling a mixture of 5-bromo-2-thenoic acid (1 mole), thionyl chloride (1.5 moles), and dry benzene under reflux for 12 h. After processing, the resulting acid chloride was distilled at 62–63°/0.25 torr, yield 95%, m.p. 40–41°; lit.[19] b.p. 126–130°/14 torr, m.p. 41–42°; $\lambda_{max}^{CHCl_3}$ 5.80 and 6.70 μm; n.m.r. data ($CDCl_3$): τ 2.24 (doublet, H-1), 2.79 (doublet, H-1, *J* 4.0 Hz).

5-Methyl-2-thenoyl chloride (**2**) was prepared by boiling a mixture of 5-methyl-2-thenoic acid (1 mole) (Aldrich Chemical Company*, m.p. 131–132°; lit.[20] m.p. 132°) and thionyl chloride (1.5 moles) in dry benzene under reflux for 8 to 10 h. After evaporation of solvent and the excess of thionyl chloride in a flash evaporator, the residue was distilled at 160°/30 torr, giving a colorless liquid that solidified completely on standing.

2-Thiopheneacrylic acid was prepared by treating 2-thiophenecarboxaldehyde with malonic acid in the presence of pyridine and piperidine by the method of King and Nord[21]; crystallized from benzene, it had m.p. 148–149°; lit.[21] m.p. 143–144°; $\lambda_{max}^{CHCl_3}$ 5.95 and 6.20 μm.

2-Thiopheneacryloyl chloride (**3**) was prepared by boiling a solution of 2-thiopheneacrylic acid (15.4 g, 0.1 mole) and thionyl chloride (17.8 g, 0.15 mole) in dry benzene (200 ml) under reflux for 12 to 15 h. After evaporation of the solvent and

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

the excess of thionyl chloride in a flash evaporator, the residue was distilled to give 2-thiopheneacryloyl chloride (15.5 g), yield 90%, b.p. 100–103°/0.2 torr that solidified on standing; lit.[22] b.p. 128–130°/6 torr; $\lambda_{max}^{CHCl_3}$ 5.80 and 6.28 μm; n.m.r. data ($CDCl_3$): τ 2.05 (doublet, H-1, J 15 Hz), 2.37 to 2.94 (multiplet, H-3), 3.62 (doublet, H-1, J 15 Hz).

5-Bromo-2-thiopheneacrylic acid was prepared by heating on a steam bath a mixture of 5-bromo-2-thiophenecarboxaldehyde (19.1 g, 0.1 mole), malonic acid (20.4 g, 0.2 mole), dry pyridine (60 ml), and piperidine (2 ml) for 2 h, and then boiling under reflux for 10 min. After filtration, and crystallization from ethanol–water, 5-bromo-2-thiopheneacrylic acid (20.9 g, 90%) was obtained; m.p. 210–211°; lit.[23] m.p. 209–210°.

5-Bromo-2-thiopheneacryloyl chloride (5) was prepared by boiling a mixture of 5-bromo-2-thiopheneacrylic acid (23.3 g, 0.1 mole), thionyl chloride (24 g, 0.2 mole), and dry benzene (200 ml) under reflux for 20 h. After processing, the resulting acid chloride was distilled; b.p. 112–115°/0.1 torr, m.p. 78–79°, yield 21.4 g (85%); $\lambda_{max}^{CHCl_3}$ 5.74 and 6.25 μm; n.m.r. data ($CDCl_3$): τ 2.14 (doublet, H-1, J 15 Hz), 2.75 (doublet, H-1, J 4 Hz), 2.85 (doublet, H-1, J 4 Hz), 3.67 (doublet, H-1, J 15 Hz).

Deltapine cotton in the form of 7s/3 yarn was purified by the method of Arthur and Mares[24] to yield cellulose (mol. wt. 700,000).

Methods. — The reactions were conducted by placing weighed yarn in a wide-mouthed Erlenmeyer flask (500 ml) fitted with a reflux condenser and a calcium chloride tube. Physical tests were performed by ASTM methods[25]. I.r. spectra of potassium bromide discs (sample:KBr, 1:300) 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[26]; the test was performed only for light-colored products.

Reaction conditions. — Dry DMF (100 to 300 ml, depending on the amount of the acid chloride used) was placed in a wide-mouthed Erlenmeyer flask (500 ml) fitted with a reflux condenser and a calcium chloride tube, 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 stirred, and a solution resulted. Cellulose (4–8 g), in the form of yarn predried at 60° for 2 h, was added to the solution, and the flask was placed in an oil bath at 80–85°. The contents of the flask were continuously stirred magnetically. After the completion of the reaction, the yarns were removed from the solution, washed twice with DMF, immersed[27] in warm methanol (50–60°) for 0.5 h, kept in 10% potassium hydrogen carbonate solution for 0.5 h, and washed thoroughly with distilled water. The yarns were then stretched, overnight at 25°, to 80–85% of their original lengths. Before being weighed or tested, all of the yarns were equilibrated for 24 h at about 50% relative humidity at 25°. The extent of the 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 chloride were obtained by altering the ratio of molar concentration of acid chloride to cellulose, or the reaction time, or both.

Reaction did not occur between cellulose and 5-bromo-2-thenoyl chloride when piperidine was used as the acid scavenger; instead, 5-bromo-*N*,*N*-pentamethylene-2-thienamide was obtained in 99% yield. The crude amide was crystallized from benzene and petroleum ether (b.p. 40–60°); m.p. 65–66°; $\lambda_{max}^{CHCl_3}$ 6.25 μm; n.m.r. data ($CDCl_3$): τ 2.94 (singlet, H-2; the chemical shifts of two protons on the thiophene ring were almost equal), 6.34 (broad singlet, H-4), and 8.34 (broad singlet, H-6).

Anal. Calc. for $C_{10}H_{12}BrNOS$: C, 43.79; H, 4.37; Br, 29.19; N, 5.10; S, 11.67. Found: C, 43.56; H, 4.30; Br, 29.00; N, 5.21; S, 11.56.

Similarly, reaction did not occur between cellulose and 5-bromo-2-thiophene-acryloyl chloride when piperidine was used as the acid scavenger; instead, 5-bromo-*N*,*N*-pentamethylene-2-thiopheneacrylamide was obtained in 90% yield. The crude amide was crystallized from benzene and petroleum ether (b.p. 40–60°); m.p. 89–90°; $\lambda_{max}^{CHCl_3}$ 6.20 and 6.35 μm; n.m.r. data ($CDCl_3$): τ 2.25 (doublet, H-1, J 15 Hz), 3.34 (doublet, H-1, J 15 Hz), 2.97 (singlet, H-2; the chemical shifts of two protons on the thiophene ring were almost equivalent), 6.37 (broad singlet, H-4), and 8.35 (broad singlet, H-6).

Anal. Calc. for $C_{12}H_{14}BrNOS$: C, 48.00; H, 4.66; Br, 26.66; N, 4.66; S, 10.66. Found: C, 47.80; H, 4.51; Br, 26.42; N, 4.60; S, 10.52.

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