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Yair Avny^a; Ron Rahman^a; Albert Zilkha^a

^a Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

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Some Complexation Reactions of Cellulosic Ethers

YAIR AVNY, RON RAHMAN, and ALBERT ZILKHA

Department of Organic Chemistry
The Hebrew University
Jerusalem, Israel

ABSTRACT

Cellulose ethers were prepared by the reaction of sodium cellulose with 1-chloromethylnaphthalene, 2-bromomethylpyridine, 2-chloropyridine, crotyl bromide, propargyl chloride, and 1-naphthyl glycidyl ether and their complexation ability was investigated. No π -complex formation with picric acid or 2,4,6-trinitrobenzene took place. Results were attributed to steric hindrance from the cellulosic backbone. Complexation of some metal salts by the crotyl and propargyl ethers was investigated. Good results were obtained with mercuric chloride, aluminum chloride, and silver nitrate when propargyl cellulose was used.

INTRODUCTION

In the course of studying complex-forming polymers, we have prepared the 2,4-dinitro- and the 2,4,6-trinitrophenyl ether derivatives of cellulose [1]. These polynitro compounds failed to yield π -complexes and the results were attributed to steric hindrance from the polymeric backbone. We have continued these studies and in the present work cellulose ethers containing donors such as naphthalene

or pyridine were prepared and their complexation with picric acid and 2,4,6-trinitrobenzene was investigated. In another part of the work we investigated the complex-forming properties of cellulose ethers containing double and triple bonds. It is well known that olefins form π -complexes with silver cations [2]. Metal acetylene complexes are involved in most catalytic addition reactions of acetylenes [3]. In some complexes, such as with silver salt [4] and platinum salt [5], the triple bond is not affected. In other cases, such as with mercury salts, addition reactions take place [6]. These addition reactions were extensively studied [6]. It was shown that mercuric chloride adds to propargyl alcohol in 55% yield [7] as well as to the corresponding methyl ether [8]. It was reported that mercuric salts undergo addition reactions with acetylenic acids and their esters [9, 10]. It was interesting to see whether cellulose ethers containing double and triple bonds could be used in order to selectively absorb metal salts from their solutions.

EXPERIMENTAL

Materials

Cellulose membrane (A. H. Thomas Co.), dialyzer tubing No. 4465-2, and scoured and bleached cotton fabric were used. DMSO (Fluka) was dried by azeotropic distillation with benzene. Tetrahydrofuran (Fluka) was dried by distillation from sodium benzophenone ketyl. 1-Chloromethylnaphthalene (Aldrich), 2-chloropyridine, crotyl bromide, and propargyl chloride (Fluka) were used. Naphthyl glycidyl ether [11] and 2-bromomethyl pyridine [12] were prepared according to literature. Sodium cellulosate was prepared as previously described [1].

Preparation of Ether Derivatives of Cellulose

Reaction was carried out in a closed glass cylinder. Sodium cellulosate of cellulose membrane (0.52 g) or 17% NaOH preswollen cotton fabric (1.50 g) was reacted with the corresponding halo or epoxy compound in DMSO (40 ml) for 24 hr, neutralized with 2% acetic acid solution, and washed with water and methanol. The cellulose ether was dried in vacuum at 65° over P₂O₅.

Complexation by the Cellulose Ether Derivatives

Extent of complexation of picric acid and 2,4,6-trinitrobenzene was determined from the decrease in their concentration in solution

as seen by UV absorption. Extent of complexation of metal salts was determined from the membrane weight gain.

RESULTS AND DISCUSSION

The etherification of cellulose by π - and n-complex-forming compounds was achieved by reacting sodium cellulosate with halo or epoxy derivatives of the corresponding compounds. Cellulose membrane and cotton fabric were used, and the sodium cellulosates were prepared by exchange reaction with sodium methoxide. Excess of sodium methoxide was removed by extraction with DMSO. The reaction with 1-chloromethyl naphthalene, 2-bromomethyl pyridine, 2-chloropyridine, crotyl bromide, propargyl chloride, and 1-naphthyloxypropylene oxide were investigated (Table 1). High sodium cellulosate D.S. was used and the extent of reaction varied with the etherification reagent. With crotyl bromide and propargyl chloride practically all the alcoholate groups reacted, leading to high ether D.S. values. With halo derivatives of pyridine, lower D.S. values were obtained. In the reaction with 1-naphthyloxypropylene oxide, graft polymerization by successive opening of the epoxide ring is also possible. In this reaction high yields were obtained only after long reaction time. No attempt to further characterize these ether derivatives was made.

Complex formation between naphthalene and the pyridine ether derivatives of cellulose and picric acid or 2,4,6-trinitrobenzene was investigated (Table 2). The corresponding reactions with naphthalene and pyridine are well known. It was found that with the two complexants, extent of complexation was negligible and most of the substituted ether groups did not react. With the 2-pyridyl methyl ether derivative the extent of reaction of the pyridine groups with picric acid was higher (12.7%). This result should be attributed to salt formation. During π -complex formation, interaction between donor and acceptor is favored when the rings are parallel and are oriented in the same way with their centers over each other [13]. It seems that the polymeric backbone interferes with such an arrangement and complex formation is prevented.

Olefin silver ion complexes are well known [2], and it was interesting to investigate the complexation ability of crotyl ether derivative of cellulose membrane. Crotyl cellulose (D.S. = 1.27) was left in silver nitrate solution but no complexation took place as seen from titration of the silver nitrate solution.

Reaction of propargyl cellulose ether (D.S. = 1.21) with several metal salts was investigated (Table 3). Extent of reaction was determined from weight gain of the cellulose ether. Control experiments with unmodified cellulose membrane were performed and absorption was corrected accordingly. Silver nitrate (6.10 mmole/g cellulosic

TABLE 1. Etherification of Sodium Cellulosate^a

Etherification	Reagent (ml)	Sodium cellulosate (D.S.)	Weight gain (%)	Ether ^b (D.S.)	Subs. alcoholate groups ^c (%)
1-Chloromethyl-naphthalene	1.0	0.50 ^d	28.8	0.33	66.0
	1.0	0.98	59.4	0.73	74.5
	1.0	0.98	58.8	0.72	73.5
	1.0	1.22	77.0	0.88	72.0
2-Bromomethyl-pyridine ^e	2.0	1.21	12.3	0.25	20.7
2-Chloropyridine	4.0	1.22	17.0	0.35	28.7
	4.0	0.94	16.3	0.34	36.2
	4.0	0.94	13.7	0.28	29.8
	4.0	0.92	9.7	0.20	21.8
Crotyl bromide	5.0	0.94	30.4	0.93	99.0
Propargyl chloride	5.0	1.28	33.7	1.36	100.0
	5.0	1.28	29.5	1.20	93.8
	5.0	1.77	41.9	1.69	95.5
1-Naphthyl-oxy pro-pylene oxide	5.0	0.97	57.2 ^f	0.50	48.5
	5.0	1.22	81.8 ^g	0.72	49.0
	5.0	1.21	126.3 ^h	1.11	92.0

^a Reaction was carried out between sodium cellulosate (membrane) (0.52 g) in DMSO (40 ml) at room temperature for 24 hr.

^b Calculated from weight gain.

^c Calculated from ether D.S. and sodium cellulosate D.S.

^d Preswelled cotton fabric (1.50 g) was used.

^e Reaction was carried in ether.

^f Reaction time 72 hr.

^g Reaction time 115 hr.

^h Reaction time 340 hr.

TABLE 2. Complexation of Picric Acid and 2,4,6-Trinitrobenzene by Ether Derivatives of Cellulose^a

Cellulose ether (g)	Ether (D.S.)	Complexed π exceptor ^b (mmole/g)	Complexed donor groups ^c (%)
Series A			
1-Naphthyl methyl ether	0.58	0.11	0.4
1-Naphthoxy 2-hydroxy propyl ether	0.72	0.12	6.5
2-Pyridyl methyl ether	0.25	0.25	12.7
Cellulose	0.00	0.10	0.0
Series B			
1-Naphthyl methyl ether	0.88	0.07	2.3
1-Naphthoxy-2-hydroxy propyl ether	0.72	0.18	7.7
2-Pyridyl methyl ether	0.25	0.00	0.0
Cellulose	0.00	0.63	0.0

^a Ether derivatives of cellulose membrane were used. Complexation was carried with 0.0005 M picric acid solution in THF (50 ml) for Series A and with 0.001 M 2,4,6-trinitrobenzene solution in THF (50 ml) for Series B.

^b Determined from the decrease of complexant concentration in solution, corrected for cellulose absorption.

^c Per cent of the total ether groups present.

TABLE 3. Complexation of Metal Salts by Propargyl Cellulose (Cellulose Membrane)^a

Metal salt	Solvent	Propargyl cellulose (g)	Ether groups (mmole)	Weight gain (%)	Adsorption by unmodified cellulose ^b (mmole/g)	Complexed salt (mmole/g)	Ether extent of complexation ^c (%)
AgNO ₃	Water	0.052	0.302	80.8	0.13	6.10	80.0
NiCl ₂	Water	0.072	0.447	4.0	0.00	0.18	2.3
CoCl ₂	Water	0.064	0.372	2.0	0.00	0.10	1.3
HgCl ₂	Water	0.046	0.271	164.1	0.00	7.86	102.8
AlCl ₃	Nitrobenzene	0.058	0.340	-	0.62	8.00 ^d	105.0
BiCl ₃	Ethanol	0.054	0.318	23.7	0.24	2.21	28.9
TiCl ₄	Benzene	0.064	0.375	0.0	1.31	0.00	0.0
SbCl ₅	Benzene	0.050	0.297	1.0	0.15	0.52	6.8

^a Propargyl cellulose (D.S. = 1.21) was left for 48 hr at room temperature in 0.05 M salt solution.

^b Calculated from weight gain.

^c Extent of complexation of the total propargyl groups.

^d Determined by titration of the AlCl₃ solution.

ether) and mercuric chloride (7.86 mmole/g) were absorbed from aqueous solution. With aluminum chloride essentially all the acetylenic bonds reacted (8.00 mmole/g). With bismuth chloride in ethanol some absorption (2.21 mmole/g) took place too. Titration of the silver nitrate and the bismuth chloride solutions confirmed the results obtained from weight gain.

Based on what is known in the literature [6], the interaction of the silver nitrate and the bismuth chloride with the triple bonds is expected to be that of π -complex formation, while that with mercuric chloride is probably of addition to the triple bonds.

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