

Note

5,6-Unsaturated derivatives of cellulose*

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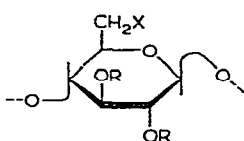
(Received May 11th, 1970; accepted for publication, June 15th, 1970)

As part of a programme for the study of the synthesis and reactivity of modified polysaccharides, we have investigated unsaturated derivatives. These compounds should readily undergo addition reactions with retention of polymeric character. We now report on 5,6-unsaturated derivatives of cellulose.

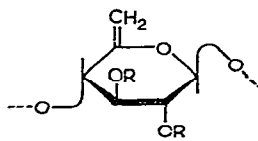
Kaverzneva and co-workers¹ described the synthesis, from iodo-tosyl precursors, of 5,6-unsaturated derivatives of cellulose which contained a high percentage of sulphur. 5,6-Unsaturated derivatives of cellulose prepared by Rogovin and co-workers² also contained a high percentage of sulphur, and, in addition, some nitrogen arising from the piperidine used to dehydroiodinate the iodo-tosyl derivatives. An additional competitive reaction involves³ the formation of 3,6-anhydro derivatives. Attempted elimination of toluene-*p*-sulphonic acid from 6-*O*-tosylcellulose and of hydrogen iodide from 6-deoxy-6-iodocellulose by using an inorganic salt (for example, lithium perchlorate) in aprotic solvents and tertiary organic bases also gave 3,6-anhydro derivatives and substitution products⁴.

In order to prevent these competing reactions, the synthesis of 5,6-unsaturated derivatives of cellulose was attempted in which the secondary hydroxyl groups of the cellulose were blocked. Benzyl and phenylcarbamoyl derivatives were chosen for this purpose because of the ease of removal of the blocking groups with retention of the unsaturation.

The required 2,3-disubstituted derivatives of cellulose (5–7) were prepared via the corresponding 6-*O*-trityl derivatives (2–4). Tosylation of compounds 5–7 was



- 1 R = H, X = OTr
- 2 R = Me, X = OTr
- 3 R = PhCH₂, X = OTr
- 4 R = PhNHCO, X = OTr
- 5 R = Me, X = OH
- 6 R = PhCH₂, X = OH
- 7 R = PhNHCO, X = OH



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|-----------------------------------|--------------------------|
| 8 R = Me, X = OTs | 14 R = Me |
| 9 R = PhCH ₂ , X = OTs | 15 R = PhCH ₂ |
| 10 R = PhNHCO, X = OTs | 16 R = PhNHCO |
| 11 R = Me, X = I | |
| 12 R = PhCH ₂ , X = I | |
| 13 R = PhNHCO, X = I | |

*Dedicated to Professor F. Micheel in celebration of his 70th birthday.

carried out with a six-fold excess of tosyl chloride in pyridine at room temperature to give compounds **8–10**, in which the degree of substitution (d.s.) was 0.94–0.99. Treatment of the sulphonates **8–10** with sodium iodide in cyclohexanone or hexane-2,5-dione afforded almost quantitative yields of the 6-deoxy-6-iodo derivatives **11–13**. Dehydroiodination with 10% methanolic potassium hydroxide then gave the unsaturated derivatives **14–16** in good yield.

EXPERIMENTAL

Double bonds were determined by the addition of bromine⁵, and trityl groups gravimetrically⁶. The contents of sulphur and iodine were determined by a modification of Schöniger's method⁷. All preparations were dried *in vacuo* at 50°.

2,3-Disubstituted derivatives of 6-O-tritylcellulose. — To microcrystalline cellulose (50 g, prepared by Dr. Kuniak of this Institute) in anhydrous pyridine (600 ml), chlorotriphenylmethane (120 g) was added with stirring. After stirring had been continued for a further 2 h at 100°, the cooled solution was treated with methanol. The precipitated 6-*O*-tritylcellulose (**1**) was collected and re-precipitated with methanol from pyridine to give a product (90 g) having a d.s. (trityl) of 0.97.

To 2 g of **1** dissolved in *N,N*-dimethylformamide (50 ml), barium oxide (2 g) and methyl iodide (25 ml) were added, and the mixture was stirred for 16 h at 40°. This procedure was repeated three times. Methanol (150 ml) was then added to the mixture, the precipitate was collected and dissolved in pyridine, and the solution was separated from the insoluble residue by centrifugation. The addition of methanol gave a precipitate which was collected, dissolved in pyridine, and reprecipitated with methanol to give 2,3-di-*O*-methyl-6-*O*-tritylcellulose (**2**, 1.5 g) [Found: MeO, 13.44. (C₂₇H₂₈O₅)_n calc.: MeO, 14.35%].

To 2 g of **1**, benzyl chloride (50 ml) and potassium hydroxide (20 g) were added. The mixture was stirred for 2 h at 120°, the cooled mixture was poured into water, and the precipitate was collected and reprecipitated from pyridine solution with water to give 2,3-di-*O*-benzyl-6-*O*-tritylcellulose (**3**, 2.9 g) [Found: C, 78.7; H, 6.15. (C₃₉H₃₆O₅)_n calc.: C, 79.1; H, 6.15%].

To 2 g of **1** dissolved in pyridine, phenyl isocyanate (12 ml) was added, and the mixture was stirred for 6 h at 100°. After cooling, the excess of phenyl isocyanate was decomposed with methanol, and the product was then precipitated and reprecipitated from pyridine with methanol to give 2,3-di-*O*-phenylcarbamoyl-6-*O*-tritylcellulose (**4**, 2.8 g) [Found: N, 4.12. (C₄₁H₃₁NO₆)_n calc.: N, 4.30%].

2,3-Disubstituted derivatives of 6-O-tosylcellulose. — The removal of the trityl groups from compounds **2–4** was effected by treating 1 g of each substance with anhydrous methanol (50 ml) and conc. hydrochloric acid (1 ml), with shaking for 24 h. The product (**5–7**) was collected, washed several times with methanol, and precipitated with methanol from pyridine.

The tosylation of compounds **5–7** was performed by dissolving 1 g of each substance in anhydrous pyridine and adding toluene-*p*-sulphonyl chloride (6 g). After

storage for 6 days at room temperature, the product was precipitated with water and purified by reprecipitation from pyridine solution. The products were as follows:

2,3-Substituent	Yield (g)	Formula	S (calc., %)	S (found, %)	D.s. (tosyl)
Me (8)	1.2	(C ₁₅ H ₂₀ O ₇ S) _n	9.30	9.21	0.99
PhCH ₂ (9)	1.5	(C ₂₇ H ₂₈ O ₇ S) _n	6.45	6.28	0.98
PhNHCO (10)	1.5	(C ₂₇ H ₂₆ NO ₈ S) _n	5.80	5.55	0.95

2,3-Disubstituted derivatives of 6-deoxy-5-iodocellulose. — The replacement of the sulphonate groups in compounds 8–10 by iodine was carried out as follows. Each tosyl derivative (1 g) was dissolved in 50 ml of cyclohexanon or hexane-2,5-dione, and dry sodium iodide (1 g) was added. The mixture was stirred for 4 h at 120°. The cooled mixture was diluted with ethanol (200 ml), and the precipitated product was filtered off. The substances (11–13), purified by dissolution in pyridine and precipitation with water, contained only traces of sulphur.

2,3-Substituent	Yield (g)	Formula	I (calc., %)	I (found, %)	D.s. (iodine)
Me (11)	0.65	(C ₈ H ₁₃ IO ₄) _n	40.02	38.10	0.95
PhCH ₂ (12)	0.70	(C ₂₀ H ₂₁ IO ₄) _n	27.20	23.76	0.87
PhNHCO (13)	0.72	(C ₂₀ H ₁₉ INO ₅) _n	24.20	20.42	0.84

2,3-Disubstituted derivatives of 6-deoxycellulose-5-enose. — Dehydroiodination of the iodo derivatives 11–13 was carried out as follows. Each substance (1 g) was treated with 10% methanolic potassium hydroxide for 48 h at 35°. The product was then filtered off and washed with methanol to neutral reaction. The products (14–16) contained no iodine and only traces of sulphur.

2,3-Disubstituent	Yield (g)	Unsaturation (%)
Me (14)	0.3	80.80
PhCH ₂ (15)	0.4	77.10
PhNHCO (16)	0.4	76.80

REFERENCES

- 1 E. D. KAVERZNEVA, V. I. IVANOV, AND A. S. SALOVA, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1949) 369.
- 2 L. S. SLETKIN, A. I. POLJAKOV, AND Z. A. ROGOVIN, *Vysokomolekul. Soedin.*, (1965) (7) 199.
- 3 D. G. DIMITROV, V. B. ATSEHJAL, L. S. ANTONJUK, L. S. CALBRAICH, AND Z. A. ROGOVIN, *Vysokomolekul. Soedin.*, (1968) (6) 1372.
- 4 F. MICHEEL AND Š. BAUER, unpublished results.
- 5 K. BAUER AND H. MOL, *Die organische Analyse*, Leipzig, 1954, p. 16.
- 6 W. M. HEARON, D. G. HIALT, AND C. R. FORDYCE, *J. Amer. Chem. Soc.*, 65 (1943) 2449.
- 7 C. PECIAR, unpublished results.