

Model Compounds of Cellulose: Trityl Ethers Substituted Exclusively at C-6 Primary Hydroxyls

DAVID M. HALL and JAMES R. HORNE, *Department of Textile
Engineering, Auburn University, Auburn, Alabama 36830*

Synopsis

Triphenylmethylcellulose (trityl cellulose) in which substitution of only the primary hydroxyls at C-6 on the cellulose chain occurs has been prepared using superdry cellulose derived from gel cellophane. The diacetate and dicarbanilate derivatives substituted exclusively at C-2 and C-3 secondary hydroxyls could then be prepared. Detritylation afforded the cellulose dicarbanilate or diacetate. Proof that no secondary substitution occurred was afforded by elemental analysis and by tosylation followed by replacement of the tosyl group with iodine. Because of the low D.P. of the cellulose and the ease with which the cellulose polymers can be cast into films, these cellulose model compounds might find utility for studying the effect of reactions at either the primary or the secondary hydroxyls of cellulose.

INTRODUCTION

A study of the reactions with cellulose are complicated by the size of the molecular chain, i.e., degree of polymerization and also by the difference in reactivities, availability, etc., of the various hydroxyl groups at C-2, C-3, and C-6 of each repeating unit of cellulose. As a result, many cellulose reactions such as crosslinking with durable press (D.P.) resins, attachment of reactive dyes, etc., are not completely understood. Model compounds, which may not take the stereo chemistry of the macromolecule into account, have been used with limited degrees of success.

Triphenylmethylcellulose (trityl cellulose) in which the hydroxyl groups at C-6 have been blocked by a triphenylmethyl group has been prepared by several workers^{1,2}; however, in each case they reported a greater degree of substitution than could be accounted for by the exclusive reaction at the C-6 primary hydroxyl group of cellulose. Stanonis³ and co-workers using a special apparatus for tritylation of cotton⁴ was able to obtain degrees of substitution greater than 1.00. If only the monomer is reacted with trityl chloride under analogous conditions, no substitution at C-2 or C-3 is usually obtained⁵; hence we felt that perhaps the reaction conditions were too severe for substitution exclusively at the sixth position with the type of cellulose used.

EXPERIMENTAL

General. All reagents were analytical grade unless otherwise indicated. Melting points were determined with a Nalge-Axelrod polarizing micro-melting point apparatus and are corrected. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory. All reactions were repeated at least three times to establish the yields and ensure that the procedure employed could be replicated.

Triphenylchloromethane (Trityl Chloride). The material was prepared by the method of Bachman⁶ and recrystallized from a 1:2 mixture of benzene and petroleum ether containing 1 ml of acetyl chloride to a melting point of 111–112°C.

Superdry Cellulose (Cellophane) Preparation (1). The gel cellophane film sheets were washed overnight in running deionized water and finally in distilled water. The sheets were air dried and then pulverized in a Wiley mill to pass a 60-mesh screen (coarser ground material gave gels in subsequent reactions; however, the results were the same). The powder (200 g) was dried at 78°C and 0.2 mm Hg in a modified drying pistol (Fig. 1) for one week, and stored in air tight containers over P₂O₅/vac until used.

Preparation of Polymer Films. The polymer was dissolved in the appropriate solvent (Table I) and filtered through a sintered glass funnel onto clean mercury in a Pyrex dish. The solutions were covered with cardboard to protect the solution from convection air currents and the solvent was slowly allowed to evaporate. In this way, films could be prepared having good uniformity and thickness. Thickness of the films could be controlled by varying polymer concentration and/or volume cast onto the mercury.

6-O-Trityl Cellulose (2). To a 1000-ml, four-necked flask fitted with a mechanical stirrer and condenser (fitted with an anhydrous calcium sulfate drying tube) which had been dried overnight in an oven at 110°C was added 30 g pulverized (60-mesh grind) and dried cellophane 1 and 700 ml anhydrous pyridine. After 1 hr at 100°C, 130 g trityl chloride (2.5 moles) was added and the reaction continued for an additional 15 hr. The clear, deep-amber solution was poured into an excess of 95% ethanol in a Waring Blender. The slurry was filtered and rinsed with 95% ethanol, and the solid precipitate was again stirred in fresh 95% ethanol. This was continued until only a faint pyridine odor was detected. After air drying,

TABLE I
Solvents and Concentrations Found Suitable for Casting Films of
Various Cellulose Derivatives

Cellulose derivative	Solvent for film casting	Concentration, g/100 ml
6-O-Trityl	acetone, chloroform, dimethylformamide	2.0
6-O-Trityl-2,3-dicarbanilate	acetone, chloroform, dimethylformamide	3.0
6-O-Trityl-2,3-diacetate	chloroform	1.0
2,3-Dicarbanilate	dimethylformamide, dioxane	2.0
6-O-Tosyl-2,3-dicarbanilate	acetone	4.0

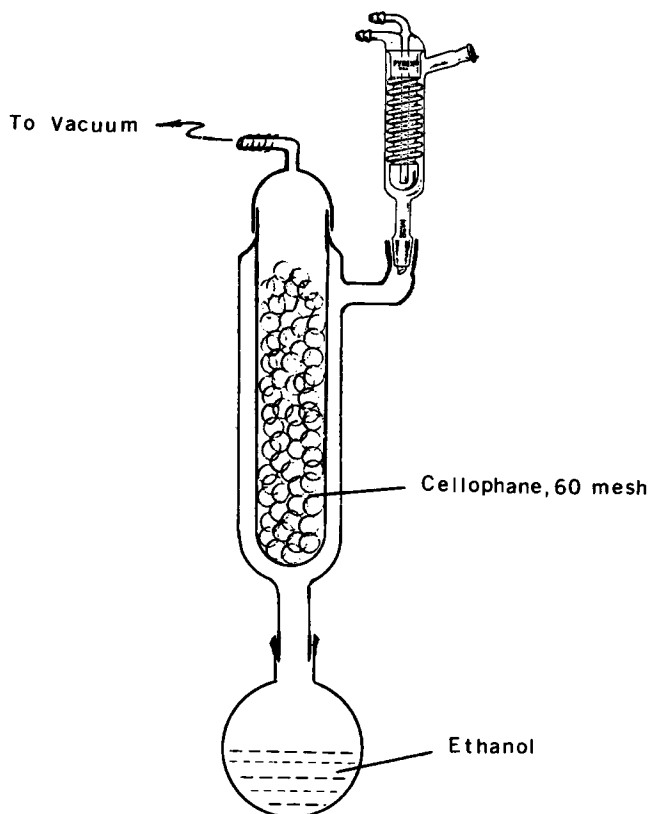


Fig. 1. Modified drying pistol employed to superdry the 60-mesh cellophane. All joints are ground glass.

the powder was extracted in a Soxhlet Extractor with 95% ethanol for 24 hr. Total yield of air-dried, pale-yellow trityl cellulose was 60 g (96%).

ANAL. Calcd for $C_{25}H_{24}O_5$ (DS = 1): C, 74.23; H, 6.00. Found: C, 74.26, H, 6.07.

6-O-Trityl-2,3-cellulose Dicarbamate (3). To a 1000-ml round-bottom flask fitted with stirrer, condenser, and drying tube (Dririte) all previously dried at 110°C overnight was added 20.5 g of 2 (which had been dried similar to that described for cellulose). Anhydrous dimethylformamide (DMF), 500 ml, was added and the solution heated to 100°C with stirring. To the clear solution was added 250 mg 1,4-diazobicyclo[2.2.2]octane catalyst followed by 37 ml phenyl isocyanate dropwise over 30 min. After 5 hr at 100°C, the hot solution was quickly poured into 1000 ml water (Waring Blender) and filtered hot. The precipitate was digested in warm (40°C) ethanol, refiltered, and air dried. The air-dried product was Soxhlet extracted with 95% ethanol for 24 hr. Yield was 30.8 g (96%).

ANAL. Calcd for $C_{39}H_{34}O_7N_2$: C, 72.9; H, 5.3; N, 4.3. Found: C, 72.7; H, 5.1; N, 4.1.

6-O-Trityl-2,3-cellulose Diacetate (4). To 10 g 6-O-trityl cellulose (2) in a 500-ml, flat-bottom flask is added 125 ml pyridine and 100 ml acetic anhydride. The solution is heated (90° C) with stirring for 8 hr. Upon cooling (25° C) the solution is poured in ethanol/water (2:1) in a Waring Blender and filtered. The sample is stirred in 95% ethanol for several hours, refiltered, and air dried. Yield was 11.5 g (95%). (The sample submitted for analysis was Soxhlet extracted 24 hr in 95% ethanol.)

ANAL. Calcd for $C_{29}H_{28}O_7$: C, 71.3; H, 5.8. Found: C, 71.3; H, 5.8.

6-Hydroxyl-2,3-cellulose Dicarbanilate (5). Detritylation of 20.5 g of 3 by the procedure of Hearon et al.¹ gave the product, 12.4 g (98%), which was purified by Soxhlet extraction in ethanol.

ANAL. Calcd for $C_{20}H_{20}O_7N_2$: C, 60.0; H, 5.0; N, 7.0. Found: C, 59.8; H, 5.0; N, 6.8.

6-Tosyl-2,3-cellulose Dicarbanilate (6). Compound 5, 5 g, was dissolved in 30 ml pyridine. *p*-Toluene sulfonyl chloride, 30 g, in 80 ml of dry pyridine was added and treated similar to that of Hearon et al.¹ to give 6 g (95%) of a pale-yellow, fibrous product.

ANAL. Calcd for $C_{20}H_{20}O_9SN_2$: S, 5.8; N, 5.0. Found: S, 5.8; N, 4.8.

6-Iodo-2,3-cellulose Dicarbanilate (7). Using the method of Hearon et al.,¹ 6 g product gave approximately 4.6 g of a bright-yellow product.

ANAL. Calcd for $C_{20}H_{19}O_8N_2I$: I, 24.9; N, 5.49. Found: I, 21.5; N, 5.0; S, 0.0. After two recrystallizations, 21.0% iodine was obtained. After six recrystallizations, 16.7% iodine was obtained.

DISCUSSION

Past workers found that the use of deacetylated cellulose as the cellulose source for tritylation seemed to afford fewer problems when preparing trityl celluloses. However, it is doubtful if all acetyl groups are removed, as a minimum value of 1% acetyl is usual for deacetylated cellulose.¹⁰ Some of the acetyl groups may be at C-6 hydroxyl. The use of cotton cellulose invariably gave insoluble products having high trityl contents. For our cellulose source, we chose gel cellophane* taken from the center of the spun sheet. The washed and air dried film had low crystallinity and a high surface to volume ratio when pulverized. The use of this material allowed us to employ mild reaction conditions and short reaction times and resulted in only the primary hydroxyl group of cellulose being substituted. Although the DP of the cellophane employed is somewhat low (about 200, kindly measured by B. S. Sprague, Celanese Research Corporation), the resulting 6-O-trityl cellulose and its derivatives could be solution cast into optically clear films having sufficient strength for further work (Table I).

The 6-O-tritylcellulose prepared was shown to have a D.S. of 1.00 by the reaction scheme similar to that employed by Hearon et al.,¹ which is shown in Figure 2. Unlike that of Hearon and his co-workers, our product gave

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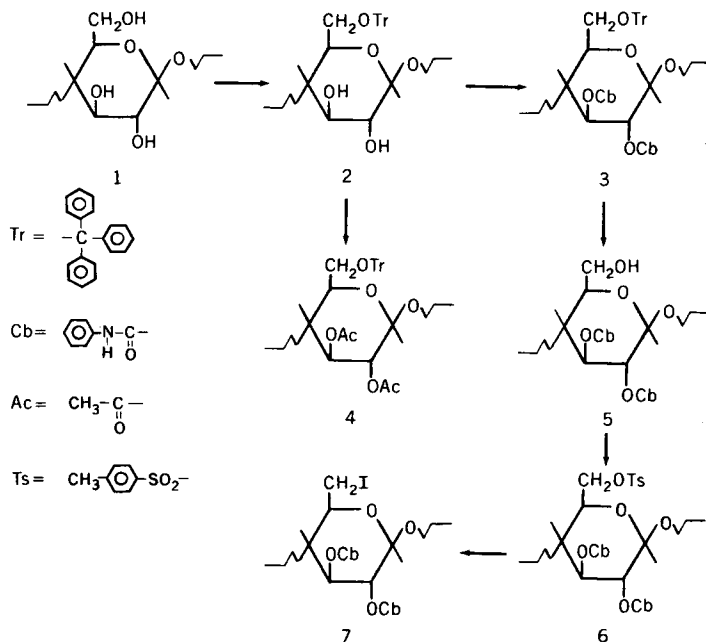


Fig. 2. Reaction scheme for trityl celluloses.

the correct elemental analysis in every case except for the 6-iodo derivative. The trityl content in trityl cellulose can be accurately calculated from the percentage of carbon found by elemental analysis.⁷ Our only deviation from a perfect analysis came when we attempted to stoichiometrically replace the tosyl group by iodine. The procedure of Hearon and co-workers calls for precipitation of the product into water. We have found that the iodo group at C-6 is apparently somewhat labile, and it is quite likely that partial cleavage of the iodo group is obtained under these conditions. We found that the iodine content of the 6-iodo derivative was reduced upon each successive recrystallization of the product. Finally, the work of Malm and co-workers⁸ suggest that it is possible for loss of tosyl to occur without entrance of iodine. Most importantly, unlike the product of Hearon et al., our product gave a negative sulfur analysis, indicating no secondary tosyl groups were present in the final product. Tosyl groups would have to be present if any tritylation of the cellulose secondary hydroxyls at C-2 and C-3 had occurred. Secondary tosyl groups as a general rule are nonreactive to iodination by acetone-sodium iodide reagent.⁹ This apparently confirms that only tritylation of the primary hydroxyl at C-6 had occurred under our reaction conditions. Our results seem to indicate that the low iodine analysis obtained by Hearon and co-workers might have been due in part to loss of iodine during recrystallization of their product or to loss of tosyl without the entrance of iodine or to residual acetate groups in their starting material. Hence, this procedure for confirming the extent of primary groups on cellulose may not be completely accurate.

In addition to the 2,3-dicarbanilate derivative of trityl cellulose, the 2,3-diacetate was also prepared which gave a product in excellent agreement with the theoretical elemental analysis. Detritylation to cellulose 2,3-diacetate by the method used for the dicarbanilate most likely resulted in some acetyl migration from secondary to primary hydroxyl during detritylation.⁸ Once air dried, the product gave a crystalline solid which resisted solvation in the usual secondary cellulose acetate solvents and produced films too hard and brittle to manipulate.

The use of dimethylformamide containing a catalytic amount of triethylenediamine (1,4-diazobicyclo[2.2.2]octane) was found to give superior results to pyridine as the reaction medium for carbanilation of cellulose with phenylisocyanate. Unlike pyridine, this catalyst has the electron pair of the nitrogens localized; hence, it is a stronger base for promoting reactions of the isocyanate. It is superior to quinuclidine, which has only one nitrogen held by the ring system. The use of the inert and water-soluble dimethylformamide assisted in recovery and purification of the resulting dicarbanilate.

SUMMARY

Using superdry cellulose of low molecular weight (cellophane), it is possible to obtain exclusive tritylation of the primary hydroxyl at C-6 uncomplicated by partial substitution at the secondary hydroxyls at C-2 and C-3 which has plagued past workers. The dicarbanilate or diacetate derivatives can be prepared followed by detritylation to give a derivative having all of the primary hydroxyls free. Except for the diacetate, the derivatives can be solution cast into clear films suitable for further study.

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References

1. W. M. Hearon, O. G. Hiatt, and C. R. Fordyee, *J. Amer. Chem. Soc.*, **65**, 2449 (1943).
2. J. Honeyman, *J. Chem. Soc.*, 168 (1947).
3. D. J. Stanonis, private communication.
4. D. J. Stanonis, W. D. King, and C. E. Esposito, *Text. Res. J.*, **35**, 44, 1965.
5. B. Helferich, *Advan. Carbohydrate Chem.*, **3**, 79 (1948).
6. W. E. Bachman, *Org. Syntheses*, **3**, 841 (1955).
7. D. J. Stanonis, in *Encyclopedia of Polymer Science and Technology*, Vol. 3, Wiley, New York, 1965, p. 541.
8. C. J. Malm, L. J. Tanghe, and B. C. Laird, *J. Amer. Chem. Soc.*, **70**, 2740 (1948).
9. J. Staněk, M. Černý, J. Kocourek, and J. Pacák, *The Monosaccharides*, Academic Press, New York-London, 1963, p. 416.
10. J. W. Green, in *Methods in Carbohydrate Chemistry*, R. L. Whistler, Ed., Vol. III, *Cellulose*, Academic Press, New York-London, 1963, p. 327.

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