

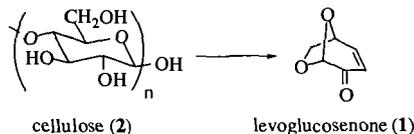
A CONVENIENT PROCEDURE FOR THE PREPARATION OF LEVOGLUCOSENONE FROM CELLULOSE AND THE CONVERSION OF LEVOGLUCOSENONE TO NOVEL CHIRAL DERIVATIVES

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INTRODUCTION

The preparation of levoglucosenone (1) by the pyrolysis of cellulose (2) under acidic conditions



has been reported recently.¹ In general, the procedures involve separating a slightly volatile liquid pyrolysate from a mixture of solids followed by purification of the liquid pyrolysate. Normally, 2-5% of pure levoglucosenone (1) is obtained.¹

The potential of levoglucosenone (1) for use in organic synthesis is exceedingly high. It is a relatively small (six carbon atoms), enantiomerically pure, rigid molecule with several important functional groups including a ketone group, a double bond conjugated with the ketone, a protected aldehyde, and two protected hydroxyl groups.¹

We have found a convenient method for converting cellulose (2) to levoglucosenone (1) in >10% yield. This procedure as well as methods to convert levoglucosenone (1) into potentially useful chiral derivatives is presented.

EXPERIMENTAL

In some runs cellulose (2) was acidified by the following pretreatment. A quantity of 20 g of cellulose (2), 600 mg of phosphoric acid, and enough methanol to cover the cellulose (2) were added to a round bottom flask and allowed to stand at room temperature for 1 h. The methanol was then removed on a rotary evaporatory under reduced pressure.

Cellulose (2) and soy oil were added to a round bottom flask containing a magnetic stirring bar. If the cellulose (2) had not been acidified by the pretreatment, an acid was also added to the flask. The flask was connected to a vacuum distillation apparatus and the pressure was lowered to 15-30 mm Hg. The reaction mixture was heated with stirring to ca. 300 °C. Within seconds levoglucosenone (1), water, and charcoal began to form and the water and levoglucosenone (1) distilled from the mixture and were condensed.

Yields of levoglucosenone (1) were determined by gas chromatography using a standard (octyl alcohol) or by direct weighing.

RESULTS AND DISCUSSION

Preparation of levoglucosenone (1).

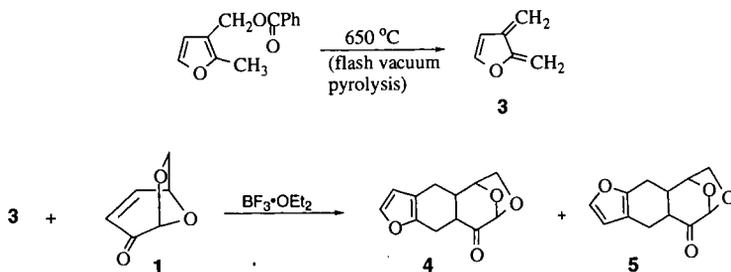
The yield of levoglucosenone (1) as a function of the temperature, the ratio of cellulose to soy oil, and the type of acid was studied. It was found that the highest yields (> 10%) of levoglucosenone (1) were obtained by using a 1:3 ratio of [cellulose (2)]:[soy oil] and a temperature of 300 °C. It was found that preacidification was not necessary: phosphoric acid could be added directly to the reaction mixture.

Conversion of levoglucosenone (1) to chiral derivatives.

Levoglucosenone (1) was converted to several derivatives which were fully characterized by infrared, mass, and ¹H and ¹³C NMR spectroscopy.

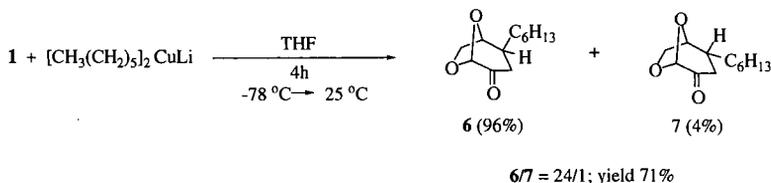
Diels-Alder reaction with the furan-based o-quinodimethane.

The preparation of (3) has been reported.²



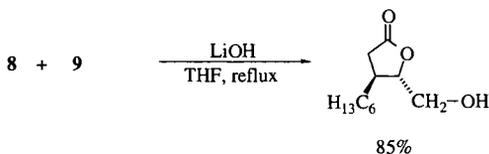
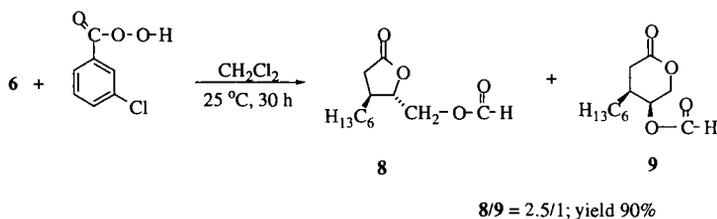
Conjugate addition of hexyl cuprate.

This procedure was based on that reported by Yamada et. al.³ The addition of pentyl cuprate to levoglucosenone (1) has been reported.⁴



Baeyer-Villiger oxidation of 6, the hexyl cuprate adduct of levoglucosenone.

This procedure was based on that reported by Murry et. al.⁵ The Baeyer-Villiger oxidation of the pentyl derivative, using different reagents, has been reported.⁴



ACKNOWLEDGEMENTS

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REFERENCES

1. (a) Witczak, Zbigniew J.; editor. *Levoglucosenone and Levoglucosans Chemistry and Applications*, Frontiers in Biomedicine and Biotechnology, Vol. 2, ATL Press, Inc., Science Publishers, Mount Prospect, IL, U.S.A., 1994. (b) see specifically Christophe Morin in ref. 1a, p. 17-21.
2. Trahanovsky, W. S.; Cassady, T. J.; and Woods, T. L. *J. Am. Chem. Soc.*, **1981**, *103*, 6691.
3. Yamamoto, K.; Ogura, H.; Jukuta, J.; Inone, H.; Hamada, K.; Sugiyama, Y.; Yamada, S. *J. Org. Chem.*, **1998**, *63*, 4449.
4. Ebata, T.; Koseki, K.; Okano, K.; and Matsushita, H.; in ref. 1a, p. 59-72.
5. Sosnowski, J. J.; Danaher, E. B.; Murry, R. K., Jr. *J. Org. Chem.*, **1985**, *50*, 2759.