Carbohydrate Research, 156 (1986) 232–235
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

Acetoacetylation of *O*-(hydroxypropyl)cellulose by 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one

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(Received December 25th, 1985; accepted for publication in revised form, February 27th, 1986)

O-(Hydroxypropyl)cellulose[1] (**1**), as well as several of its derivatives[2–4], form both thermotropic and lyotropic mesophases. This unique property allows liquid crystallinity to be induced by either heat or solvent in the same polymer. Therefore, this type of polymer is more advantageous than one which forms only a thermotropic or lyotropic mesophase. The aim of the present work was to synthesize a new derivative of **1** that could potentially exhibit these characteristics.

Diketene is used in the preparation of many acetoacetates and heterocycles[5,6]. Unfortunately, the lachrymatory nature, extreme reactivity, and instability of diketene at room temperature are detrimental to its efficient use. However, diketene reacts with acetone to form a 1:1 adduct, 2,2,6-trimethyl-4*H*-dioxin-4-one (**2**), in excellent yield[7,8]. This diketene–acetone adduct, which is stable at room temperature and is a nonlachrymatory liquid, is known to decompose via a retro-Diels–Alder process at temperatures above 100° to yield acetone and acetylketene. Recently, it has been shown[7] that the resulting acetylketene has exceptional ability to acetoacetylate a variety of nucleophiles.

O-(Acetoxypropyl)cellulose (**3**) was readily prepared by the acetoacetylation of *O*-(hydroxypropyl)cellulose (**1**). The reaction may be performed either neat or in the presence of an inert organic solvent such as *N*-methyl-2-pyrrolidinone (NMP) or dimethyl sulfoxide. The same reaction vessel and conditions were employed in either instance; the procedure using NMP as the solvent for **1** is described.

EXPERIMENTAL

O-(Acetoacetoxypropyl)cellulose. — *O*-(Hydroxypropyl)cellulose (**1**, 3.6 g, ~0.01 mol, nominal molecular weight 100,000 from Aldrich Chemical Co.), dried for ~4 h at 70°, was transferred to a 250-mL, one-neck round-bottom flask. To this was added 150 mL of NMP (Fisher Scientific Co.) which was dried over 4Å molecu-

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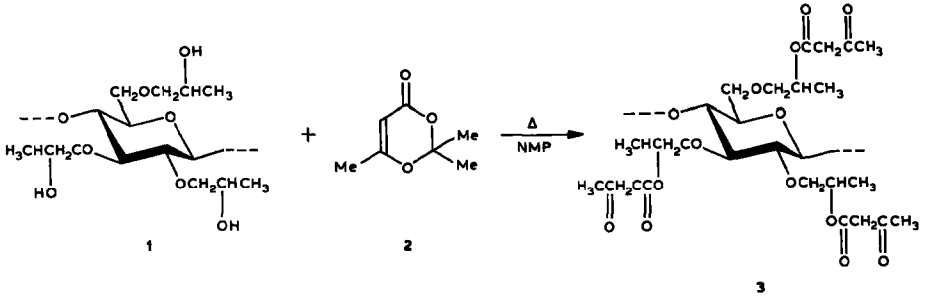
0008-6215/86/$ 03.50

lar sieves and used without further purification. Nitrogen was bubbled through the mixture for 30 min while it was rapidly stirred. The flask was then stoppered and stirring continued for an additional 15 h to enhance dissolution. The mixture was transferred to a 250-mL, three-neck round-bottom flask equipped with a nitrogen inlet-tube, a thermometer, and a Dean–Stark trap. 2,2,6-Trimethyl-4*H*-1,3-dioxin-2-one (**2**, 8.6 g, ~0.06 mol, twice distilled) was added and the mixture was stirred for 20 min while nitrogen was bubbled through it. The excess of **2** was used to ensure reaction with as many hindered hydroxyl groups as possible. The flask was lowered into an oil bath, the mixture was stirred and heated to 100–120°, and acetone (3.3 g) was distilled off over a 1-h period. Throughout the course of the reaction, nitrogen was continuously bubbled through the mixture. Efficient removal of acetone is necessary to provide good quality of product[7]. After the reaction was complete, the reddish-brown mixture was poured into a large excess of iced distilled water. The *O*-(acetoacetoxypropyl)cellulose (**3**) separated as a yellowish, sticky mass. It was washed several times with copious amounts of water to remove reactants and then purified by dissolution in acetone and reprecipitation with water. The sample was dried under vacuum for 48 h.



RESULTS AND DISCUSSION

A thin film of **3** was cast from a 5% solution in acetone onto a KBr plate and the i.r. spectrum of the polymer sample was recorded with a Perkin–Elmer 281 B i.r. spectrophotometer. The strong absorption bands at 1710 and 1735 cm^{-1} (Fig. 1, curve I) are indicative of the carbonyl functionality of the acetoacetate. Similarly, a thin film was made from a solution of **1** in distilled water; its i.r. spectrum (Fig. 1, curve II) exhibits a broad hydroxyl peak in the 3500–3400 cm^{-1} region. The decreased intensity of the same peak in the spectrum of **3** is indicative of incomplete substitution.

^{1}H-N.m.r. spectra were obtained with a Bruker WM 250 n.m.r. spectrometer operating at 250 MHz. Solutions (~3%) were prepared in $CDCl_3$. The ^{1}H-n.m.r. spectrum shows singlets at 3.41 p.p.m., characteristic of the $-COCH_2CO-$ group, and 2.24 p.p.m., characteristic of the $-COCH_3$ group[9].

Signals for protons of the terminal methyl group of the ether occur at 1.10

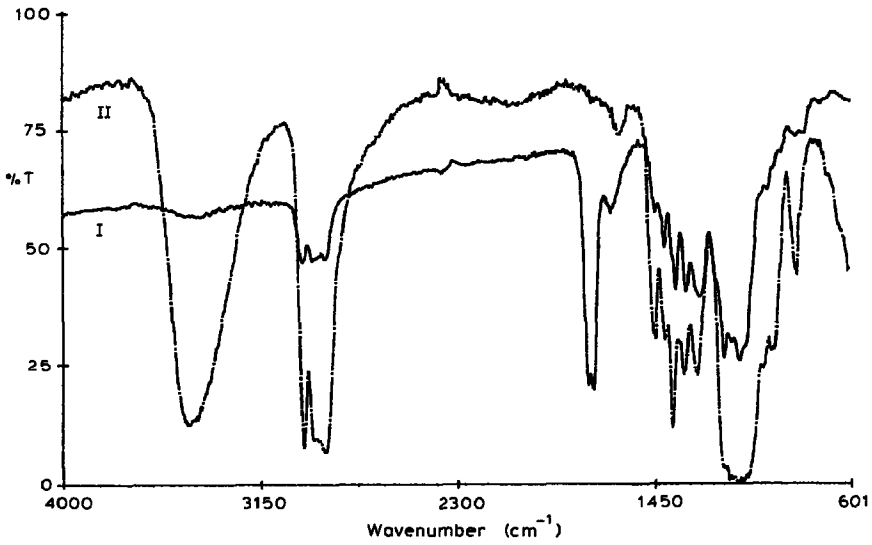


Fig. 1. I.r. spectra of compounds **3** (I) and **1** (II).

and 1.22 p.p.m. The appearance of two signals for the terminal methyl groups of the propoxy substituent indicates that the chemical environment of these groups is not identical throughout the polymer molecule. This difference may be the result of incomplete acetoacetylation, or may reflect the differing extension of the branches. A doublet centered at 1.22 p.p.m. is attributed to the methyl protons on the substituted propoxy units with splitting by the adjacent methine proton. A singlet at 1.92 p.p.m., in conjunction with the smaller one at 4.98 p.p.m. results from keto–enol tautomerism of the acetoacetoxy group. A broad singlet at 5.02 p.p.m. is attributed to the methine proton and has been observed by Lavinis[10] in acetylated **1**. All other protons give rise to a broad resonance centered at 3.48 p.p.m. There was no evidence from the n.m.r. spectrum of acetyl ketene dimer.

The degree of esterification was determined by saponification and titration. A slightly modified procedure of the ASTM test-method for cellulose acetate[11] was employed. A 0.5-g sample of dried **3** was dissolved in 75 mL of acetone and 10 mL of M NaOH was added. The hydrolysis was performed for 4 h at room temperature with constant stirring. The excess of base was backtitrated with previously standardized sulfuric acid, using phenolphthalein as the indicator. The value of 2.2 for the degree of substitution (esterification) obtained in this manner was based on a value[12] of 3.4 for the molar etherification of **1**. Integration of the n.m.r. spectrum, giving a value of 2.0 for the molar degree of esterification, further supported the value obtained by saponification.

Compound **3** in bulk melts readily to show a crystalline to liquid-crystalline transition (C→LC) at ~120° and a liquid-crystalline to isotropic transition (LC→I) at ~170°. It exhibits green reflection colors at room temperature which are charac-

teristic of cholesteric mesophases with pitch sizes in the visible-wavelength region.

The product **3** is soluble in acetone, acetic acid, and dichloromethane, and forms mesophases in the latter two solvents. These mesophases display the high optical rotations associated with cholesteric cellulose-based mesophases. The polymer was unchanged after 3 months at 0° under nitrogen.

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