Note

Preparation of cellulose carbonate*

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The reaction of ethyl chloroformate, in the presence of triethylamine, with pyranoid compounds containing vicinal diequatorial hydroxyl groups is known to give *trans*-five membered cyclic derivatives[1]. Thus, methyl 4,6-*O*-benzylidene-α-D-glucopyranoside gives methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-carbonate, and methyl 2,6-di-*O*-(methylsulphonyl)-α-D-glucopyranoside gives the 3,4-cyclic ester. According to the reaction conditions, methyl 4,6-*O*-benzylidene-α-D-glucopyranoside can also give the 2,3-di-*O*-ethoxycarbonyl or the 2- and 3-mono esters. The 2,3-*trans*-fused cyclic carbonates showed characteristic absorptions in the 1810–1840 cm^{-1} region of the i.r. spectrum; the *O*-ethoxycarbonyl group absorbed at 1750 cm^{-1}.

The carbonate derivatives of starch, dextran, and dextrin have been reported[2]; these are soluble in methyl sulphoxide. The cellulose carbonate described herein is, so far as we are aware, the first insoluble polymer converted into its carbonate derivative.

DISCUSSION

In these preparations, the cellulose carbonate may contain both *trans*-2,3-cyclic carbonate structures, and *O*-ethoxycarbonyl (acyclic carbonate) groups, derived from the reaction of ethyl chloroformate with either a *trans*-2,3-hydroxyl group or with the individual hydroxyl groups on carbon atoms 2, 3, and 6 of the D-glucopyranose residues respectively.

In all the preparations of cellulose carbonate, three major absorption bands at 1835, 1810, and 1750 cm^{-1} were observed. The band at 1750 cm^{-1} corresponds to the acyclic *O*-ethoxycarbonyl group, and the bands at 1810 and 1835 cm^{-1} are characteristic of the *trans*-fused cyclic carbonate[1]. The ratio of the absorbances at 1835 to 1810 cm^{-1} was fairly constant, values lying between 0.70 and 0.90.

In order that a high percentage of the *trans*-cyclic-2,3-carbonate may be obtained, it is evident that all components of the reaction must be dry (Table I, a and e). This is probably due to water, acting as a nucleophile, being able to open the cyclic carbonate group in the presence of triethylamine. Furthermore, it has been shown that *trans*-cyclic-2,3-carbonates undergo ring opening with methanol, toluene thiol, and piperidine in the presence of triethylamine to give mixtures of the 2- or 3-substituted derivatives[5]; hence, solvents possessing –OH, –SH, –NH, or –NH$_2$ groups should not be used in the preparation of cellulose carbonate.

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Prolonging the reaction time beyond 10 min reduced progressively the yield of *trans*-2,3-cyclic carbonate (Table I, a). This is probably due to slow opening of the cyclic carbonate rings in some way, thus decreasing the cyclic carbonate group content and relatively increasing the acyclic content.

Such a polar aprotic medium as methyl sulphoxide, and such a strong base as triethylamine appear to be essential (Table I, b and c). When either of these compounds was replaced by 1,4-dioxan, the amounts of *trans*-cyclic carbonates were reduced to very low values. Methyl sulphoxide should not be replaced by *N,N*-dimethylformamide as an alternative aprotic medium (Table I, d). The cyclic carbonate groups appear to be gradually opened by *N,N*-dimethylformamide in the presence of triethylamine.

Other chloroformates, such as methyl, phenyl, and benzyl chloroformates, used in amounts equimolecular to that of ethyl chloroformate, are not as effective as ethyl

TABLE I

QUANTITATIVE I.R. SPECTROSCOPY OF CELLULOSE CARBONATE PREPARATIONS

Conditions of preparation	*Ratio[a] of optical absorbances at 1750 and 1810 cm^{-1}*	*Relative substitution[b]*
a. Standard conditions and variation of reaction time (in min)		
10	0.36	100
30	0.79	52
60	0.93	31
240	0.89	28
b. Variation of TE[c] concentration (% of standard amount)		
50	0.78	32
25	0.73	1
0	0.60	1
c. Variation of DMSO concentration (% of standard amount)		
75	1.12	51
50	0.63	41
25	0.44	16
0	0.26	10
d. Use of DMF		
In place of DMSO	0.28	39
In place of DMSO, PD in place of TE	0.00	3
e. Use of undried solvents		
Dry reaction solvents, undried washing solvent	0.96	45
Undried reaction solvent, undried washing solvent	0.72	23
f. Use of other chloroformates		
MCF	0.63	21
BCF	0.30	7
PCF	2.03	4

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[a] Absorbance at 1750 cm^{-1} (ethoxycarbonyl) relative to absorbance at 1810 cm^{-1} (cyclic carbonate). [b] Cyclic carbonate content relative to that in product from standard conditions. [c] Abbreviations as in text.

chloroformate (Table I, f.). This is probably the result of electronic and steric factors affecting the attack of the nucleophile on the carbonyl carbon atom, as a consequence of altering the ester part of the chloroformate.

Thus, according to the findings, the best set of conditions for producing a cellulose carbonate with a high percentage of cyclic carbonate is that described for a. in Table I with the 10-min reaction time. In the product, the ratio of acyclic to cyclic carbonate groups is at a minimum, whilst a good percentage of cyclic carbonate is present.

The percentage of carbonate groups determined by titration and elemental analysis of the coupled product agreed quite well within experimental errors. However, these percentages are much lower than that determined by using quantitative i.r. spectroscopy calibrated with dextran carbonate. This could well be due to a non-specific opening of the *trans*-cyclic carbonate rings by water which is present in large excess compared with that of ammonia. However, the ring-opening reactions of ammonia and benzylamine to give urethane links further demonstrate the initial presence of the *trans*-2,3-cyclic carbonate group.

EXPERIMENTAL

Preparation of cellulose carbonate. — Cellulose (Sigmacell, particle size 38 μm, Sigma Chemical Co., 200 mg) was suspended in dry methyl sulphoxide (DMSO, 2 ml), dry 1,4-dioxan (PD, 0.3 ml), and dry triethylamine (TE, 1.6 ml), and the mixture was stirred for 5 min at 0°. Ethyl chloroformate (ECF, 3.2 ml) was added dropwise over 12 min with stirring, and the mixture left to react with stirring for a further 10 min. The product was immediately washed, by stirring with a Waring blender and centrifuging, with dry PD (10 × 15 ml); the final supernatant diluted 1:1 with water showed a pH of 7.5. Washing was continued with ethanol (3 × 15 ml) and diethyl ether (3 × 15 ml), and the product was then dried.

Quantitative i.r. spectroscopy in the range 2000–1600 cm^{-1} was carried out on this (Table I, a) and subsequently described products as a KBr disc. The percentage of units converted to cyclic carbonate was estimated to be 53.8% using a calibration curve constructed from soluble dextran carbonate, the carbonate content of which had been determined[3] as 38.5% by hydrolysis with barium carbonate and titration[4]. Similar titration in the case of cellulose carbonate gave uninterpretable results, probably due to occlusion of barium hydroxide in the polymer.

Further samples of cellulose were derivatised in ways similar to the above standard conditions, but using different reaction times (10–240 min), or replacing partially or totally TE and DMSO with additional PD, keeping the final volume constant (Table I, a, b, and c, respectively). The standard conditions were also modified by the use of dry *N*,*N*-dimethylformamide (DMF, 2 ml) in place of DMSO, with and without replacement of the TE with additional PD to give the usual final volume (Table I, d). It was observed that treatment of cellulose carbonate (100 mg) with DMF (10 ml), water (10 ml), and TE (0.25 ml) for 24 h at 20° resulted in the complete loss of the i.r. peak at 1810 cm^{-1}.

The use of a wet washing process was also investigated for cellulose carbonate prepared by both the standard reaction conditions and the same conditions but with undried solvents. After reaction with ethyl chloroformate, the mixtures were neutralised with 6M hydrochloric acid, washed with ethanol and then with ether, and dried (Table I, e). Finally, the standard conditions were used with equimolar proportions of benzyl, methyl, or phenyl chloroformates (BCF, MCF, PCF, respectively) in place of ECF (Table I, f).

Reaction of cellulose carbonate with ammonia and benzylamine. — Cellulose carbonate prepared under anhydrous conditions (200 mg) was stirred with 0.36M aqueous ammonia (5 ml) for 3 h at 20°, and aliquots of the supernatant were titrated with 0.1M hydrochloric acid. The centrifuged product was washed, dried, and analysed by i.r. spectroscopy in the standard manner. *Anal.* Found: C, 41.6; H, 5.7; N, 0.8; this nitrogen content corresponds to a minimum cyclic carbonate group content of 11.7%, compared with 16.7% based on titration. The total cyclic carbonate content available for reaction, based on i.r. analysis together with the appropriate calibration curve with dextran carbonate, was 37.6%. A similar coupling was carried out with benzylamine, and the percentage of cyclic carbonate groups based on titration was 11.4%, compared with 14.7% based on nitrogen content.

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