1057. *Carbonic Esters of Sucrose. Part II.*[1] *The Polymerisation of O-Alkyloxycarbonylsucroses.*

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O-Ethoxycarbonylsucroses polymerise, with elimination of diethyl carbonate and ethanol, to form cross-linked resins when heated in the presence of an alkaline catalyst. The influence of the degree of substitution of the ester and its catalyst content upon polymerisation are discussed. A method for the direct preparation of an alkali-catalysed monomer from sucrose in high yield is described.

IN Part I [1] the thermal polymerisation of a partially substituted *O*-ethoxycarbonylsucrose containing a trace of alkali was reported. Although the formation of condensation-polymers from aliphatic [2,3] and aromatic [3,4] carbonic esters is well known, and addition-polymers have been prepared from unsaturated *O*-alkyloxycarbonyl-carbohydrates [5–7] no other example of the thermal condensation of a carbohydrate carbonate to yield a cross-linked resin appears to have been published.

The polymerisation of *O*-ethoxycarbonylsucroses occurs most rapidly at temperatures above about 145°, and preferably under reduced pressure, which aids the removal of volatile by-products. The process is strongly catalysed by traces of alkali and inhibited by acids. To study the limitations imposed by the degree of substitution (D.S.) of the monomer, varying concentrations of sodium hydrogen carbonate were added to neutral ester samples (Table 1). With an increasing D.S., the setting-times produced by the same catalyst concentration were found to increase considerably. Likewise, the higher the D.S., the smaller the accelerating effect produced by a given rise in catalyst concentration.

TABLE 1.

Influence of degree of substitution and catalyst content upon the polymerisation of *O*-ethoxycarbonylsucroses.

Average D.S. of monomer	Setting time (min. at 160° *in vacuo*) at varying concns. (% w/w) of $NaHCO_3$ 0·01	0·1	0·25	0·5	Average OEt content of polymers (%)
3·4 [a]	40	4	—	3	14·8
4·7 [b]	50	20	6	5	25·0
5·7 [c]	90	60	45	25	27·3
7·9 [d]	N.S.	N.S.	N.S.	N.S.	—

[a] Prepared from sucrose and 5 mol. of ethyl chloroformate, followed by ether-fractionation,[1] and removal of catalyst with air-dried cellulose powder (see Experimental). [b] Isolated from the ether extract of a 5 mol. preparation.[1] [c] Isolated from the ether extract of a 20 mol. preparation. [d] Prepared by further acylation of monomer, with D.S. 5·7, in pyridine.[1] N.S. = Not set in 6 hr.

As already indicated,[1] sufficient of an alkaline impurity to catalyse subsequent polymerisation may in certain circumstances accompany the *O*-ethoxycarbonylsucroses during their isolation from the preparation mixture. The solvent used for extraction has a profound effect upon the alkali content of the recovered esters (Table 2). Ether achieved a partial fractionation of the esters, but no catalyst passed into the ether phase. Benzene and chloroform each dissolved all of the syrup precipitated from a 5 mol. preparation, but differed greatly in their capacity to extract alkaline matter

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[1] Part I, preceding paper.

[2] Carothers and Van Natta, *J. Amer. Chem. Soc.*, 1930, **52**, 314.

[3] Reynolds and Van Den Berghe, U.S.P. 2,789,509, 2,789,964—5, 2,789,967—8, 2,789,970; Reynolds and Dunham, U.S.P. 2,789,966, 2,789,969, 2,789,971—2/1957; Caldwell, U.S.P. 2,799,666/1957.

[4] Schnell, *Angew. Chem.*, 1956, **68**, 633; *Trans. J. Plastics Inst.*, 1960, **28**, 143.

[5] Muskat and Strain, U.S.P. 2,384,115/1945, 2,385,930/1945, 2,399,285/1946, 2,399,287/1946.

[6] Schwartz, Brown, and Tally, U.S. Dept. Agr., Bur. Agr. and Ind. Chem. Mimeo. Circ. Ser. 1952, AIC, 339, p. 9 (*Chem. Abs.*, 1953, **47**, 10,486).

[7] Zief, *J. Amer. Chem. Soc.*, 1950, **72**, 1137.

simultaneously. When benzene, the most effective of the three solvents, was used the proportion of alkali extracted decreased with increasing degree of substitution of the *O*-ethoxycarbonylsucroses, thus suggesting an association between the catalyst and the free hydroxyl groups of the esters. Furthermore, none of the sodium salts likely to be found in the reaction mixture was comparably soluble in benzene alone. Percival[8] has shown that sucrose itself readily forms addition compounds with potassium hydroxide, for example $C_{12}H_{22}O_{11},3KOH$, whilst in aqueous solution, particularly at low temperatures, acid carbonic esters of the type $C_{12}H_{21}O_{11}\cdot CO_2^-Na^+$ may exist.[9] The lower affinity of the higher *O*-ethoxycarbonylsucroses for alkali may account for the reduced influence of the total catalyst concentration upon setting time at higher D.S., already noted (Table 1).

Ethyl chloroformate is most economically employed in the preparation of sucrose esters of low D.S., and substitution at higher levels becomes increasingly less efficient (Table 2 and Part I [1]). The lowest D.S. at which an *O*-ethoxycarbonylsucrose becomes sufficiently hydrophobic to be isolated by solvent extraction appears to be 3. Such a trisubstituted ester possesses the additional advantage of a very short setting time *in vacuo* when suitably catalysed. The weights of the rapidly setting monomers obtained respectively from experiments B, D, and E (Table 2) represent yields of 74, 47, and 28% based on sucrose, and yields of only 55, 31, and 29% based on the chloroformic ester used. Incomplete separation of product from the saline phase, and only partial utilisation of sucrose, owing to the preferential formation of higher esters in the chloroformate phase, were believed to be responsible for these relatively low yields. By increasing the concentration of the aqueous alkali employed in the preparation, and by modifying the addition procedure to avoid its initial dilution, an optimum " salting-out " of triester, by the sodium chloride produced, was obtained. The tendency to polysubstitution in the ethyl chloroformate phase was minimised by adding an excess of light petroleum to the reaction mixture, to decrease the solubility of the trisubstituted ester in the reagent. By these means, alkali-catalysed *O*-ethoxycarbonylsucrose, with an average D.S. of about 3, was caused to be precipitated from the preparation mixture in 80% yield, based on ethyl chloroformate.

TABLE 2.

Influence of extraction solvent upon the alkali-content of *O*-ethoxycarbonylsucroses.

Expt.	Reagents (mol.) per mol. of sucrose	Extraction solvent	Yield (g.) from 50 g. of sucrose	Average D.S.	% Alkali (calc. as $NaHCO_3$)	Setting time (min.) at 160° *in vacuo*
A	10	C_6H_6	100	4·8	0·0003	105
B	5	C_6H_6	66	3·8	0·13	4
C	5	$CHCl_3$	88	3·7	0·0009	40
D	5	Et_2O	31 (extract)	4·6	Nil	Not set in 40 hr.
			40 (insol.)	3·3	0·24	4
E	3·3	C_6H_6	24	3·5	0·23	4

The polymerisation of " tri-*O*-ethoxycarbonylsucrose " at 160° *in vacuo* produced a liquid distillate which infrared analysis has shown to consist of almost equal proportions (w/w) of ethanol and diethyl carbonate. It seems likely that the polymerisation process itself is a simple alkali-catalysed transesterification (i), with the elimination of ethanol, and that the diethyl carbonate also isolated arises by simultaneous alkali-catalysed ethanolysis (ii) of some remaining *O*-ethoxycarbonyl groups. Examples of the direct elimination of diethyl carbonate between two *O*-ethoxycarbonyl groups to yield a carbonate polymer as in (iii) are known,[3] but such reactions appear to occur only at much higher temperatures (250°) and often only in the presence of a more specific catalyst, *e.g.*, tetrabutoxy titanium. On the other hand, *O*-ethoxycarbonyl groups have been shown to undergo alcoholysis very readily under certain conditions (see below). The polycarbonate from

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[8] Percival, *J.*, 1935, 648.

[9] Smidt and Thamsen, *Acta Chem. Scand.*, 1956, **10**, 1172.

a trisubstituted *O*-ethoxycarbonylsucrose retains an average of about 1·5 *O*-ethoxycarbonyl groups per sucrose unit.

The availability of free hydroxyl groups for a type (i) reaction will decrease with the extent of substitution in the monomer, until, in the case of octa-*O*-ethoxycarbonylsucrose no polymerisation occurs under normal conditions. It is also likely that in the more highly substituted esters (average D.S. 5—7) only those hydroxyl groups remain which, by virtue of steric hindrance or low acidity, are the least reactive. Such esters therefore show a much reduced affinity for an alkaline catalyst and velocity of polymerisation.

$$\mathrm{XO{\cdot}CO_2Et + XOH \longrightarrow XO{\cdot}CO_2X + EtOH} \qquad \text{(i)}$$

(where X is a substituted sucrose radical)

$$\mathrm{XO{\cdot}CO_2Et + EtOH \longrightarrow XOH + Et_2CO_3} \qquad \text{(ii)}$$

$$\mathrm{2XO{\cdot}CO_2Et \longrightarrow XO{\cdot}CO_2X + Et_2CO_3} \qquad \text{(iii)}$$

An approximately trisubstituted *O*-benzyloxycarbonylsucrose, obtained by solvent fractionation, has also been polymerised in the presence of alkaline catalyst. The process was more sluggish but was accompanied by less simultaneous alcoholysis than in the case of the corresponding *O*-ethoxycarbonyl ester. A distillate consisting chiefly of benzyl alcohol and dibenzyl carbonate in 4 : 1 ratio (w/w) was obtained.

Whilst the full evaluation of these polymers has not been completed, their susceptibility to alkaline hydrolysis (Table 3) is an obvious practical disadvantage. As expected, the problem is most serious with the less hydrophobic polymers from low-substituted esters, but variations apparently connected with the polymerisation conditions also occur. These variations are being studied. Hydrolysis of the polymers was progressive, even with a catalytic amount of alkali, presumably owing to the instability of sodium hydrogen carbonate in boiling solution.

TABLE 3.

Stability of polymerised *O*-ethoxycarbonylsucroses towards boiling alkaline soap solution.*

D.S. of monomer	Setting time (min.) at 160° *in vacuo*	% Polymer recovered after boiling for ½ hr.	D.S. of monomer	Setting time (min.) at 160° *in vacuo*	% Polymer recovered after boiling for ½ hr.
5·7	75	93	3·5	4	14
4·8	105	90	3·0	70	19
3·8	40	72	2·9	25	0
3·7	4	35			

* As used for the screening of potential textile finishing agents (Dr. J. Honeyman, personal communication).

The final cross-linking stage of the polymerisations may be carried out under pressure at about 160°. Hard, tough, moulded samples were produced from a mixture of partly polymerised " tri-*O*-ethoxycarbonylsucrose " with an equal weight of asbestos fibre as a " filler." Air-dried fillers based on cellulose inhibit the polymerisation to an extent probably related to their effective surface area (cellulose powder > cotton cloth > paper). This inhibiting effect, due to adsorption of the polymerisation catalyst on to the cellulose, may be prevented either by exhaustive drying of the filler or by its pre-treatment with very dilute aqueous sodium hydrogen carbonate.

The *O*-ethoxycarbonylsucroses undergo de-esterification by the lower primary, and to a smaller extent secondary, alcohols in the presence of an alkaline catalyst. t-Butyl alcohol is inactive. The reaction is reversible [10] but the equilibrium may be displaced to the right by the continuous crystallisation of sucrose. Thus, whilst catalysed *O*-ethoxy-

$$\mathrm{XO{\cdot}CO_2Et + ROH \xrightleftharpoons{NaHCO_3} XOH + RO{\cdot}CO_2Et}$$

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[10] Theobald, Part III, following paper.

carbonylsucrose (D.S. 3·3) suffered complete alcoholysis in butan-1-ol alone during 6 hr. at 100°, the addition of dimethyl sulphoxide, to maintain homogeneous conditions, prevented any significant decomposition. Methanol, on the other hand, de-esterified the derivative even in the presence of the additional solvent.

EXPERIMENTAL

Polymerisations of O-*Ethoxycarbonylsucroses Catalysed by Sodium Hydrogen Carbonate.*—The esters (*ca.* 5 g., accurately weighed) were dissolved in warm t-butyl alcohol (50 ml.) and treated with the requisite weight of sodium hydrogen carbonate in water (10 ml.), and the solutions evaporated *in vacuo*. Dehydration of the syrups was completed by two evaporations with benzene.

The polymerisations were carried out at 12 mm. in 50 ml. flasks heated in an oil-bath at 160°, and the time taken for all movement of the resinous mass just to cease was recorded as the "setting time" (reproducible to $\pm 5\%$ on samples of *ca.* 2—5 g.). Polymerisation was much slower below about 145° (a sample taking only 15 min. to set at 150° required 90 min. at 140°). Reduced pressure accelerated the polymerisation (15 min. at 12 mm. against 45 min. at 760 mm.).

Solvent Extraction of O-*Ethoxycarbonylsucrose Preparations.*—The preparations were conducted on a 50-g. scale by the general method described in Part I,[1] with 10, 5, or 3·3 mol. of the reagents per mol. of sucrose. Ether-fractionation of the 5-mol. preparation followed the procedure already given.[1] Benzene and chloroform extractions were carried out by decanting the saline phase from the precipitated esters, dissolving the latter in the solvent (500 ml.), and extracting the former with more solvent (2 × 250 ml.). The combined organic extracts were then immediately dried by azeotropic distillation at reduced pressure (fresh solvent being added if necessary), filtered, and finally evaporated to clear syrups.

Estimation of Alkaline Catalyst in Esters.—The syrups (3—5 g. approx., accurately weighed) were dissolved in warm ethanol (50 ml.) and diluted to 100 ml. with distilled water. The solutions were titrated potentiometrically against 0·01N-sulphuric acid, and the end-points determined graphically (*ca.* pH 5·5). The alkali-contents were calculated as % of sodium hydrogen carbonate (w/w).

Modified Preparation of Approximately Trisubstituted O-*Ethoxycarbonylsucrose.*—A vigorously stirred solution of ethyl chloroformate (46 ml, 3·3 mol.) in light petroleum (b. p. 100—120°; 250 ml.) was cooled in ice and treated dropwise with sucrose (50 g.) in 3N-sodium hydroxide (176 ml., 3·6 mol.). During the addition (4 hr.), the temperature was kept at 0—2°, and the level of the stirrer was adjusted to avoid serious dispersion of the precipitated esters. After overnight stirring, with the temperature rising slowly, the syrup was separated and dissolved in benzene (500 ml.), and the solution evaporated under reduced pressure at 60° to remove water. The process was repeated with further benzene until all turbidity had disappeared, and the final benzene solution was filtered and evaporated. This gave 69 g. (83·5% based on sucrose; 80% based on ethyl chloroformate) of a material with setting time 6 min. at 160° *in vacuo* (Found: OEt, 24·8%, equiv. to D.S. 3·1; sulphated ash, 1·1%, equiv. to Na 0·36%; free alkali by potentiometric titration, 0·06% w/w, calc. as $NaHCO_3$).

Separation of the heavy syrupy esters from the saline and the light petroleum phase was facilitated by fitting the reaction vessel with a wide-bore stopcock. A "constant-head" device contributed to regular alkali-addition.

Examination of the Distillate from the Polymerisation of O-*Ethoxycarbonylsucroses.*—The catalysed derivative (D.S. 3·25) from a modified preparation was dried for 4 hr. *in vacuo* at 60° and weighed (6·62 g.). The flask containing the dried syrup was connected to a weighed trap, the apparatus evacuated, and the trap immersed in acetone–carbon dioxide. Heating of the monomer was begun (oil-bath at 160°), and volatile products were rapidly condensed. After ½ hr. (setting time was 5 min.) heating was stopped and the distillate weighed (1·26 g.). Qualitative tests indicated the presence of diethyl carbonate and ethanol in the liquid. The infrared spectrum (700—4000 cm.$^{-1}$) was identical with that of an artificial 1 : 1 w/w mixture of diethyl carbonate and ethanol containing a trace of moisture.

Preparation of Approximately Trisubstituted O-*Benzyloxycarbonylsucrose.*—Sucrose (20 g.) was caused to react with benzyl chloroformate (40 g., 4 mol.) and 3N-sodium hydroxide (78 ml., 4 mol.) at 0° by the general method of Part I.[1] After stirring overnight, the mixture was shaken with ether (200 ml.) to give three layers: ether (upper), syrup (middle, fraction A), and saline (lower).

The ether extract was further fractionated by addition of light petroleum (b. p. 60—80°; 20 ml.) to yield a syrup (fraction B) and a supernatant layer (fraction C). Chloroform-extraction of the saline layer removed only a negligible quantity of oil. The major fractions were dried ($CaSO_4$) (the syrups in chloroform solution), and the recovered *O*-benzyloxycarbonyl-sucroses heated at 120°/10^{-4} mm. for 1 hr. to remove volatile impurities. Yields were: A (4·2 g.) (Found: C, 58·6; H, 5·8%; av. D.S.; 3·3); B (11·3 g.) (Found: C, 59·0; H, 5·6%; av. D.S., 3·4); C (11·5 g.) (Found: C, 62·2; H, 5·5%; av. D.S., 5·5).

Polymerisation of O-*Benzyloxycarbonylsucrose* (D.S. 3·3).—The derivative (A) (1·28 g.) was homogeneously mixed with sodium hydrogen carbonate (0·5% w/w) by the same procedure as for *O*-ethoxycarbonylsucroses. Polymerisation (at 165°/10^{-2} mm.) and condensation of volatile products were carried out as before. The setting time (25 min.) was longer than that shown by a corresponding *O*-ethoxycarbonyl derivative. The distillate (0·22 g.) smelled of benzyl alcohol. Its infrared spectrum corresponded broadly to that of a 4 : 1 (w/w) mixture of benzyl alcohol and dibenzyl carbonate, but contained additional minor peaks at 1706 and 1725 cm.$^{-1}$.

The polymer (Found: C, 48·9; H, 5·0%) possessed similar solubility characteristics to those of polymerised *O*-ethoxycarbonylsucrose.

Hydrolysis of Polymerised O-*Ethoxycarbonylsucroses by Boiling Soap Solution*.—The polymers were finely ground and heated *in vacuo* at 160° for 50% of their previous setting times to complete cross-linking and to remove any volatile impurities, being afterwards reground if necessary. Samples (2 g.) were then heated for ½ hr. under reflux (stirring) with 50 ml. portions of a soap solution (0·5% w/v of " Sunlight " soap and 0·2% w/v of anhydrous sodium carbonate in water). The suspensions were diluted with water (50 ml.) and filtered whilst hot (suction), and the recovered polymers were washed with hot water (100 ml.) and dried to constant weight at 60° *in vacuo*. In one case (that from monomer with D.S. 4·8; Table 3), the recovered polymer was rehydrolysed, and the same percentage loss obtained, showing no significant change in the reactivity of the polymer after one hydrolysis treatment.

Preparation of Asbestos-filled Discs from O-*Ethoxycarbonylsucroses*.—An approximately tri-substituted derivative was polymerised at 160° *in vacuo* for 80% of its normal setting time (10 min.). The viscous resin was cooled, powdered, and distributed as evenly as possible throughout an equal weight of asbestos wool by kneading the mass with a small volume of chloroform. After being air-dried, the material was compressed (2 ton/sq. in.) in the centre of a steel washer separating two electrically heated (160°) platens. The hydraulic press was opened twice to add further solid and permit the escape of volatile products. Heating and pressure were continued for ½ hr.; a hard disc (sp. gr. *ca.* 1·4), unaffected by 24 hours' immersion in chloroform, was obtained.

On a large scale, the partial polymerisation of a rapidly setting derivative is preferably carried out at a somewhat lower temperature (*e.g.*, 140°), as the slower reaction allows more even heating of the sample.

Use of Cellulose Fillers with O-*Ethoxycarbonylsucroses*.—Catalysed " tri-*O*-ethoxycarbonyl-sucrose " (setting time 5 min. at 160° *in vacuo*), when shaken for a few minutes in chloroform solution with an equal weight of air-dried cellulose powder (" Ashless, for chromatography "), suffered complete loss of catalyst and did not polymerise in contact with the cellulose or when recovered (98%) as a syrup from the chloroform phase. Other forms of cellulose showed less severe prolongation of setting time, *e.g.*, cotton wool (55 min.), cotton cloth (20 min.), and filter-paper (6 min.).

Cellulose powder, dried *in vacuo* at room temperature over phosphoric oxide or at 160°, had no inhibiting effect on polymerisation. Cellulose powder, stirred with 1% w/v aqueous sodium hydrogen carbonate, collected, and air-dried, could also be used in the preparation of discs.

Alcoholysis of O-*Ethoxycarbonylsucroses*.—Samples (1—2 g.) of " catalysed " *O*-ethoxy-carbonylsucrose (D.S. 3·3) obtained from a modified preparation, were heated with various alcohols (10—20 parts by vol.) on the steam-bath under reflux for 6 hr. The solutions were then examined chromatographically (Part I [1]), with the initial ester as reference material.

De-esterification to sucrose was complete in methanol, ethanol, and butanol, but only partial in propanol. Crystallisation of the sucrose was particularly rapid from butanol. Repetition of the experiments in the presence of dimethyl sulphoxide (10 parts) caused complete alcoholysis only in the case of methanol. Attack was partial with ethanol, less with propanol, and negligible with butanol.

In the absence of additional solvent, propan-2-ol and butan-2-ol caused only partial de-esterification of the same derivative in 6 hr. A new substance, R_F 0·43 (butan-1-ol–pyridine–water 10 : 3 : 3 v/v), was detected in the former case but was not isolated. t-Butyl alcohol was without effect. Alkali-free ester samples were not de-esterified by methanol.

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