631. *Sucrose Derivatives. Part II.* Some Silyl and Cyanoethyl Ethers and a Hepta-acetal.*

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Selective substitution of sucrose has been achieved by using chlorotricyclohexylsilane. 1,10-Divinyloxydecane with sucrose yielded mainly a hepta-acetal. Tri-*O*-vinylsucrose has been produced by transvinylation of sucrose in tetrahydrothiophen dioxide (tetramethylene sulphone). Octa-*O*-(2-cyanoethyl)sucrose was isolated from the mixture produced by repeated reaction of sucrose with acrylonitrile.

Trimethylsilylation of various sugar derivatives[1,2] yields materials of high thermal stability from which the substituent trimethylsilyl groups can be removed under mild neutral conditions. Octa-*O*-(trimethylsilyl)sucrose,[3,4] for example, results from the reaction of an excess of chlorotrimethylsilane with sucrose in dry pyridine. Reaction of sucrose with an excess of chlorotriphenylsilane afforded a hexa-*O*-(triphenylsilyl)sucrose. Attempts to increase the degree of substitution were unsuccessful and it appears that the bulky nature of the substituent triphenylsilyl groups prevents further substitution. This contention was supported by the fact that reaction of sucrose with an excess of chlorotricyclohexylsilane[5] afforded only a trisubstituted derivative.

On treatment with lead tetra-acetate in pyridine this trisubstituted derivative rapidly consumed 3 mol. of oxidant, followed more slowly by a further 2—3 mol. due to overoxidation. Sucrose behaved identically and has been shown by Hockett and Zief[6] to be susceptible to overoxidation under these conditions. An initial rapid uptake of 3 mol. of lead tetra-acetate by the derivative would be expected only if three primary hydroxyl groups of the sucrose molecule were substituted. Attempts to produce 6,1′,6′-tri-*O*-substituted sucrose derivatives usually result in complex mixtures.[7] Hexaphenyldisiloxane and tricyclohexylsilanol were formed in the foregoing reactions, respectively, owing to hydrolysis of the Si–Cl bond by atmospheric moisture which is difficult to exclude under the reaction conditions.

Hexa-*O*-(triphenylsilyl)- and tri-*O*-(tricyclohexylsilyl)-sucrose were not readily

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* Part I, *J.*, 1962, 3158.

[1] Hedgley and Overend, *Chem. and Ind.*, 1960, 378.

[2] Ferrier and Singleton, *Tetrahedron*, 1962, **18**, 1143.

[3] Chang and Hass, *J. Org. Chem.*, 1958, **23**, 773.

[4] Henglein, Abelsnes, Henecka, Lienhard, Nakhre, and Scheinost, *Makromol. Chem.*, 1957, **24**, 1.

[5] Nebergall and Johnson, *J. Amer. Chem. Soc.*, 1949, **71**, 4022.

[6] Hockett and Zief, *J. Amer. Chem. Soc.*, 1950, **72**, 2130.

[7] Lemieux and Barrette, *Canad. J. Chem.*, 1960, **38**, 656; McKeown, Serenius, and Hayward, *ibid.*, 1957, **35**, 28.

hydrolysed in boiling aqueous methanol,[1] and a mixture of ethanol–ether–4N-sodium hydroxide at 65° was required to regenerate the sucrose.

The preparation of sucrose derivatives containing vinyloxy-groupings is attractive because of their potential use as monomers in polymerisation and copolymerisation. 1,10-Divinyloxydecane was prepared by transetherification and condensed with sucrose in dimethylformamide under conditions previously reported[8] to be suitable with other vinyl ethers. Elemental and sugar analyses of the product were consistent for a hepta-*O*-1-(10-vinyloxydecyloxy)ethylsucrose. Since only 6·5 vinyloxy-groupings per molecule could be detected a small proportion (<1 in 14) of the acetal substituents could by cyclised. The acetal was completely hydrolysed by N-hydrochloric acid at 70° in 1 hour. The hydrolysate contained *inter alia* glucose, fructose, and acetaldehyde which resulted from hydrolysis of either $-O{\cdot}CHMe{\cdot}O-$ or $-O{\cdot}CH=CH_2$ groups in the acetal.

Reppe[9] was unable to prepare vinyl derivatives of sucrose because of the extensive alkaline degradation encountered when using acetylene and potassium hydroxide at high temperatures. Transetherification in a suitable solvent with a mercuric acetate catalyst seemed the best approach. Unfortunately use of a basic solvent such as pyridine or dimethylformamide would inactivate the catalyst. Transvinylation of sucrose in dimethyl sulphoxide at 100° for 96 hr. was attempted with 12 mol. of butyl vinyl ether and mercuric acetate. Paper chromatography of the reaction mixture indicated the presence of a sugar derivative which moved near the solvent front (R_{sucrose} 9·0 in butanol–ethanol–water) and fluoresced under ultraviolet light. The catalyst was inactivated and the reaction mixture poured into water and continuously extracted with ether. Attempts to separate the mixture of sucrose vinyl ethers and high-boiling decomposition products of dimethylsulphoxide in the ether extract were unsuccessful. Although the formation of the decomposition products was avoided by conducting the reaction at 65° the yield of vinylsucroses (0·22 g. from 10 g. of sucrose) after 28 hours' heating with ethyl vinyl ether was extremely small. The observation that tetrahydrothiophen dioxide was a good solvent for sucrose at 140° provided a solution to the present problem and this solvent should prove extremely useful generally in sucrose chemistry.

The products of transvinylation in this sulphone were separable into ether-soluble and chloroform-soluble fractions. The former solvent extracted the more highly substituted sucrose vinyl ethers (average 4·5 vinyl groups per molecule), while the latter afforded relatively pure tri-*O*-vinylsucrose(s). Sugar analysis, vinyl determination, and elemental analysis all indicated 3·1—3·2 vinyl groups. This vinylsucrose consumed 1·8 mol. of periodate, indicating that preferential substitution of the hydroxymethyl groups in sucrose had not occurred and that probably the reactive 2-hydroxyl group of the glucose portion is substituted.

MacGregor and Pugh[10] succeeded in cyanoethylating starch and cellulose almost completely by treating them with acrylonitrile in aqueous alkali and later refluxing the product with acrylonitrile containing only a trace of alkali. When a similar method was applied to sucrose three cyanoethylations were required to produce octa-*O*-(2-cyanoethyl)-sucrose. Di-(2-cyanoethyl)ether was encountered as a by-product, together with copolymers of sucrose and acrylonitrile. The polymers were insoluble in chloroform but soluble in acetone from which they were fractionally precipitated by addition of water.

EXPERIMENTAL

*Preparation of Hexa-*O*-(triphenylsilyl)sucrose.*—All operations were carried out under rigorously anhydrous conditions. A solution of chlorotriphenylsilane (45·4 g., 0·154 mole) in pyridine (200 ml.) was added during 20 min. to a stirred solution of sucrose (5·2 g., 0·015 mole) in pyridine (100 ml.). The mixture was shaken at room temperature for 20 hr. and thereafter

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[8] Barker, Brimacombe, Jarvis, and Williams, *J.*, 1962, 3158.

[9] Reppe, *Annalen*, 1956, **601**, 81.

[10] MacGregor and Pugh, Proc. XIth Int. Congress Pure Applied Chem., 1947, p. 123.

refluxed for 4 hr. at 130° (bath). Pyridine hydrochloride was removed, the filtrate concentrated, and the solid residue extracted with toluene–light petroleum (b. p. 40—60°) (170 ml.; 7 : 10 v/v). The residual solid (11·6 g.) was washed with methanol and after drying had m. p. 222—224°, and an infrared spectrum identical with that of hexaphenyldisiloxane. The toluene–light petroleum extract was concentrated to a viscous syrup which was dissolved in ether (50 ml.), and the product was precipitated by addition of methanol (300 ml.). This operation was repeated; the precipitated solid (15·5 g.), after drying, had m. p. 105—110°, $[\alpha]_D^{20}$ +22° (*c* 3·5 in $CHCl_3$) [Found: C, 76·2; H, 5·7%; *M* (Barger[11]), 1828. $C_{120}H_{106}O_{11}Si_6$ requires C, 76·1; H, 5·65%; *M*, 1893], $\nu_{max.}$ 1429, 1105 (Si–Ph[12]), and ~3600 cm.$^{-1}$ (OH stretching).

Preparation of 6,1′,6′-*tri*-O-(*tricyclohexylsilyl*)*sucrose*.—A solution of chlorotricyclohexylsilane[5] (1·9 g.), m. p. 100—101°, in dry pyridine (20 ml.) was added during 10 min. to a stirred solution of sucrose (0·21 g.) in pyridine (30 ml.). After shaking for 20 hr. at room temperature, the mixture was heated at 140° (bath) for 4 hr., and on cooling poured into ether (100 ml.). The pyridine hydrochloride was filtered off and the filtrate concentrated to dryness under reduced pressure. The sucrose derivative was extracted with methanol (50 ml.), the methanol removed, and the solid residue extracted with ether to yield the *product* (0·52 g.), m. p. 150—160°, $[\alpha]_{5461}^{21}$ +21° (*c* 1·1 in pyridine) [Found: C, 67·8; H, 10·3%; *M* (Barger[11]), 1118. $C_{66}H_{118}O_{11}Si_3$ requires C, 67·6; H, 10·15%; *M*, 1172]. The methanol-insoluble residue (1·1 g.) had m. p. 177—178° and was identified as tricyclohexylsilanol (lit.,[5] m. p. 176—177°).

The foregoing silyl derivatives were hydrolysed in 1 : 1 ethanol–2N-hydrochloric acid at 95° for 2 hr. and the sugar content of the neutralised hydrolysates determined.[13] These contents were 15% (calc. 18%) and 26% (calc. 29%), respectively.

Oxidation of 6,1′,6′-*Tri*-O-(*tricyclohexylsilyl*)*sucrose by Lead Tetra-acetate*.—The sucrose derivative (12 mg.) in pyridine (15 ml.) was treated with a 0·0691N-lead tetra-acetate[14] solution in pyridine (4·5 ml.) at 10°, and the volume rapidly adjusted to 25 ml. Aliquot parts (4 ml.) of this solution were removed at intervals and run into a solution (10 ml.) containing sodium iodide (0·2 g.) and sodium acetate (2 g.). The iodine liberated was titrated against 0·005N-sodium thiosulphate. The uptake of oxidant was 3 mol. (25 min.), 4 mol. (70 min.), 5 mol. (4·5 hr.), 5·8 mol. (16 hr.). Sucrose (35 mg.) behaved similarly when oxidised.

Paper Chromatography.—Chromatograms were run on Whatman No. 1 paper irrigated with pentyl alcohol–pyridine–water (1 : 1 : 1) or butan-1-ol–ethanol–water (4 : 1 : 5) and sprayed with naphtharesorcinol or silver nitrate

Preparation of 1,10-*Divinyloxydecane*.—Dry diethyl sebacate (30·1 g.) in tetrahydrofuran (300 ml.) was added in 1 hr. to a stirred suspension of lithium aluminium hydride (12 g.) in tetrahydrofuran (250 ml.), and the mixture was refluxed for a further 30 min. After cooling, ethyl acetate (250 ml.) was added, followed by 2N-hydrochloric acid (300 ml.). When recovered from the upper layer and recrystallised from ethanol–water, the decane-1,10-diol (18·4 g., 90%) had m. p. 71—72° (Chuit[15] gives 72·2°).

Decane-1,10-diol (13·4 g., 77 mmoles) and butyl vinyl ether (77·7 g., 777 mmoles) were heated under reflux with mercuric acetate (0·72 g.) at 100° for 48 hr. The suspension was filtered and flash-evaporated by dropwise introduction into a flask at 90°/12 mm. The fraction of b. p. 92—98°/0·5 mm. obtained by distillation of the residue was redistilled at 0·2 mm. A fraction (2·8 g.) of the *diether* which showed no infrared OH stretching absorption but strong absorption at 1610—1640 cm.$^{-1}$ was collected (Found: C, 74·3; H, 11·4. $C_{14}H_{26}O_2$ requires C, 74·4; H, 11·5%).

Reaction of 1,10-*Divinyloxydecane with Sucrose*.—1,10-Divinyloxydecane (1·02 g.) was added to a solution of sucrose (0·168 g.; molar ratio, sucrose : ether, 1 : 9) in dimethylformamide (4·8 g.) which was cooled in ice before addition of concentrated hydrochloric acid (0·001 ml.) in dimethylformamide. After 12 hr. at 18° the white jelly produced was finely chopped, and the reaction flask shaken for a further 3 hr. After removal of the supernatant liquid the residual jelly was washed with dimethylformamide (6 × 10 ml.), ethanol (3 × 10 ml.), and light petroleum (10 ml.). After drying *in vacuo* (P_2O_5) the product (0·681 mg.) showed $[\alpha]_D^{26}$

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[11] Barger, *Proc. Chem. Soc.*, 1903, **19**, 121; *J.*, 1904, **85**, 286.

[12] Bellamy, " Infra-red Spectra of Complex Molecules," Methuen, London, p. 277.

[13] Shaffer and Hartmann, *J. Biol. Chem.*, 1921, **45**, 365.

[14] McClenahan and Hockett, *J. Amer. Chem. Soc.*, 1938, **60**, 2061.

[15] Chuit, *Helv. Chim. Acta*, 1926, **9**, 264.

$+14\cdot85°$ (*c* 0·674 in chloromethyl cyanide). Its sucrose content, determined[8] as for other acetals, corresponded to 6·82 mol. of combined 1-(10-vinyloxydecyloxy)ethyl residues (Found: C, 67·6; H, 10·6. $C_{110}H_{204}O_{25}$ requires C, 67·8; H, 10·9%). *Hepta*-O-[1-(10-*vinyloxydecyloxy*)-*ethyl*]*sucrose* showed only weak infrared absorption at 3400 cm.$^{-1}$ but strong absorption at 1620—1660 cm.$^{-1}$. The latter arose from the 6·49 vinyl groups found to be present in the sucrose acetal by Siggia and Edsberg's method[16] with chloromethyl cyanide as solvent. In control experiments the chloromethyl cyanide did not affect the end-point. A hydrolysed acetal solution gave a positive reaction for acetaldehyde when tested with 4-hydroxybiphenyl–concentrated sulphuric acid.

Vinylation of Sucrose.—Sucrose (9·8 g., 29 mmoles) was dissolved in tetrahydrothiophen dioxide (63·4 g.) at 140° and the cooled solution mixed with butyl vinyl ether (50·6 g., 506 mmoles) and mercuric acetate (1·0 g.). The stirred solution was refluxed at 115° for 70 hr. then filtered and flash-evaporated at 120°/15 mm. The residual solvent was distilled off at 120°/5 mm. Most of the thick dark amber gum left dissolved in ether and the remainder (6·8 g.) in chloroform. The ether-soluble fraction contained two or three components of R_F 0·85—0·95 in the butanol-containing solvents; the chloroform-soluble fraction contained the fastest-moving component only. Infrared analysis showed that the ether-soluble fraction absorbed more strongly at 1640—1720 cm.$^{-1}$ and less strongly at 3400 cm.$^{-1}$ than did the chloroform-soluble fraction. The sugar contents corresponded to combination with 4·55 vinyl groups for the ether-soluble and 3·09 vinyl groups for the chloroform-soluble fraction. Determination of unsaturation[16] revealed 3·16 vinyl groups per molecule of chloroform-soluble fraction (Found: C, 52·3; H, 7·4%. A vinyl sucrose having an average of 3·25 vinyl groups requires C, 52·1; H, 6·8%).

The chloroform-soluble fraction (128·9 mg.) under the conditions described by Dyer[17] consumed 1·44 mol. of periodate in 18 hr. and 1·865 mol. in 96 hr. Sucrose, under identical conditions, consumed 2·89 mol. in 18 hr. and 3·10 mol. in 96 hr.

Cyanoethylation of Sucrose.—Acrylonitrile (6 g., 113 mmoles) was added to sucrose (18·5 g., 54 mmoles) in water (75 ml.). Sodium hydroxide (8 g.) in water (25 ml.) was added to the solution, which was shaken for 5 hr. and then neutralised with hydrochloric acid. After evaporation *in vacuo* the residual solid was extracted with methanol, ethanol, and acetone, and the combined extracts were evaporated. The residue was refluxed with an excess of acrylonitrile (30 g.) and a small amount (0·2 g.) of sodium hydroxide in water (0·5 ml.) for 8 hr. After neutralisation the organic layer was separated and washed with water (3 × 20 ml.) at 50°, then heated at 50°/5 mm. Part of the product (3·01 g.) was again cyanoethylated for 4 hr. with acrylonitrile (18 g.) and sodium hydroxide (*ca.* 0·05 g.) in water (0·3 ml.). The new product (Found: C, 58·3; H, 7·6; N, 14·7%), isolated as previously, was fractionated into a chloroform-soluble (2·67 g.), and an acetone-soluble fraction (4·03 g.). The former had $[\alpha]_D^{16\cdot4}$ $+29\cdot1°$ (*c* 0·086 in $CHCl_3$) and contained C, 58·8; H, 6·5; N, 17·8%. The latter had $[\alpha]_D^{15\cdot6}$ $+6\cdot25$ (*c* 0·120 in acetone) and contained C, 61·9; H, 6·00; N, 21·1%. Part (1 g.) of the chloroform-soluble fraction was dissolved in acetone (12 ml.) and water was added, yielding as successive precipitates fractions (I) (44·2 mg.) and (II) (370 mg.). Fraction (III) (198 mg.) was recovered from the remaining solution by evaporation. Fraction (II) was *octa*-O-(2-*cyanoethyl*)*sucrose*, $[\alpha]_D^{18\cdot8°}$ $+36\cdot4°$ (*c* 0·08 in $CHCl_3$) (Found: C, 56·6; H, 6·1; N, 14·8%; *M*, 745. $C_{36}H_{46}Ns_8O_{11}$ requires C, 56·4; H, 6·1; N, 14·6%; *M*, 766).

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[16] Siggia and Edsberg, *Ind. Eng. Chem., Analyt. Edn.*, 1948, **20**, 762.

[17] Dyer, " Methods of Biochemical Analysis," Interscience Publ., Inc., New York, 1956, Vol. III, p. 112.