Method B. The *N*-alkyl substituted heterocyclic amine (0.01 mole) was mixed with 0.005 mole of a 1,10-dihalodecane and heated on a steam bath without solvent for from 1.5 to 14 hr. The solid which resulted was recrystallized from absolute alcohol.

Method C. The appropriately substituted 1,10-dipiperidinodecane (0.005 mole) was refluxed with 0.1 mole of methyl iodide in 10 ml. of absolute ethanol for from 17 to 22 hr. The solids produced were recrystallized from ethanol or isopropyl alcohol to a constant melting point.

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Formation of Isomaltulose in Enzymatic Dextran Synthesis

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During a study of the formation of dextran from sucrose, using enzyme preparations from the bacterium *Leuconostoc mesenteroides* (NRRL B-512F), two new sugars were isolated as by-products of the reaction. One of these, the crystalline disaccharide leucrose, was briefly described in a preliminary note[2] in 1952 and later shown[3] to be 5-*O*-α-D-glucopyranosyl - D - fructose. From the leucrose mother liquors a small amount of another disaccharide was obtained analytically and chromatographically pure, although not crystalline. It could easily be distinguished from isomaltose by paper chromatography, but its phenylosotriazole was identical with that of isomaltose, thereby essentially establishing its structure as isomaltulose, 6-*O*-α-D-glucopyranosyl-D-fructose. This conclusion was reported[4] at the 1954 Symposium on Carbohydrates in Relation to Biology and Medicine, where the rotation of the sugar was given as +98°. Because of the pressure of other work, publication of the details of these studies was delayed. In the meantime, an elegant method for the 90% conversion of sucrose into crystalline isomaltulose by the action of *Enterobacteriaceae* was reported by Weidenhagen and Lorenz in 1957.[5,6] Their product with an optical rotation of $[\alpha]_D^{20} = 97.2°$ was given the trivial name palatinose. Seeding a water-methanol solution of our lyophilized isomaltulose with crystals supplied by Dr. Weidenhagen resulted in complete conversion of our product to crystalline isomaltulose having an x-ray diffraction pattern identical with that of the Weidenhagen sample. In the present paper we wish to complete our studies on the by-products of the enzymatic dextran synthesis by reporting the details of this work on isomaltulose.

EXPERIMENTAL

Isolation of isomaltulose. In work already described,[3] 600 g. of sucrose was enzymatically converted to a mixture of products from which were separated 213.3 g. of dextran, 60.4 g. of crude crystalline leucrose, 33.4 g. of tri-, tetra- and higher oligosaccharides, and 32.9 g. of a disaccharide mixture (in the mother liquor from the leucrose crystallization). Aliquots (250 mg.) of this latter mixture were separated on a cellulose powder column (3 × 118 cm.), using 3:2:1.5 butanol:pyridine:water[7] as eluant. Isolation of the various fractions showed the 32.9 g.-mixture to consist of 19.1 g. leucrose, 4.3 g. isomaltose, and 9.5 g. of a disaccharide later shown to be isomaltulose.

Final purification of the isomaltulose was accomplished by applying 150 mg. of the fairly pure material obtained from the cellulose column to large sheets ($18^1/_4'' \times 22^1/_2''$) of heavy filter paper (Whatman No. 3)[8] and by employing the butanol:pyridine:water mixture again as the developing solvent. The 100 mg. of disaccharide obtained by water elution of the proper area was shown by further paper chromatography to be a single substance. $[\alpha]_D^{25} + 103°$ (*c* 1.9; water). No mutarotation was observed in 4 hr.; this result is in accord with the report of Weidenhagen and Lorenz.[5,6]

Anal. Calcd. for $C_{12}H_{22}O_{11}$: C, 42.12; H, 6.45. Found: C, 42.22; H, 6.52.

Properties of isomaltulose. The lyophilized isomaltulose obtained in our work crystallized completely in wet methanol on seeding with a sample provided by Dr. Weidenhagen. X-ray diffraction patterns showed the two crystalline compounds to be identical.

By the Somogyi method,[9] the sugar showed 50% of the reducing power of fructose on a molar basis. Subjected to paper chromatography (butanol:pyridine:water) it moved just ahead of maltose in a position approximately one-third of the distance between maltose and sucrose. When sprayed with urea-phosphoric acid reagent, chromatograms of isomaltulose gave the greenish-blue spot characteristic of fructose disaccharides.

Determination of fructose in isomaltulose by the anthrone method of Wise *et al.*[10] gave an unusually high result (121% of theory). This yield was accounted for when further studies showed that the new sugar produced hydroxymethylfurfural at a more rapid rate than either fructose or sucrose.

Attempts to establish the ketose nature of the reducing moiety by the Willstätter-Schudel alkaline hypoiodite oxidation were unsatisfactory. The 0.346 mole of iodine consumed was much higher than would be expected of a ketose. This behavior was explained when it was demonstrated that isomaltulose can be readily transformed by alkali into compounds chromatographically indistinguishable from isomaltose, glucose, fructose, and possibly mannose. A disaccharide spot believed to be the 2-epimer of isomaltose is also evident.

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Structural Studies. Isomaltulose was hydrolyzed by heating for 1 hr. in 0.25N hydrochloric acid. Paper chromatography showed approximately equal amounts of glucose and fructose.

Isomaltulose (68 mg.) was converted to 63 mg. of the phenylosazone, which, when crystallized from wet ethyl acetate, melted at 203–204° (cor.). The phenylosazone of isomaltose was found to melt at 201–202° (cor.). Both osazones were cleaved with sodium periodate to yield the crystalline 1,2-bisphenylhydrazone of mesoxalaldehyde. Oxidation of the phenylosazone of isomaltulose with copper sulfate gave 23 mg. of a phenylosotriazole [m.p. 179–180° (cor.)], shown by mixed melting-point test and x-ray diffraction patterns to be identical with the phenylosotriazole prepared from pure isomaltose.

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Synthesis of 4-(2,3-Epoxypropoxy)phenyltrimethylsilane

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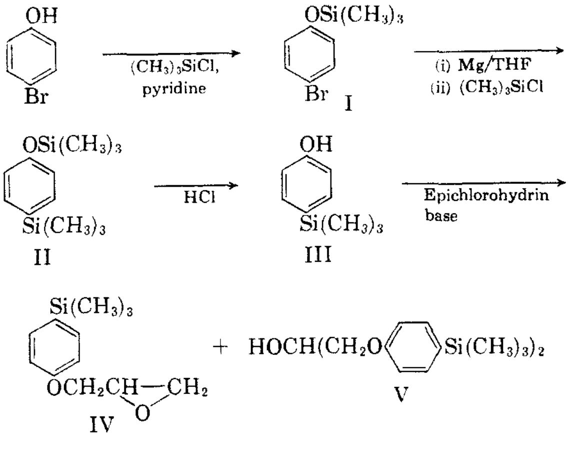
Organosilicon compounds containing epoxide groups are of quite recent origin. Martin[1] reported the preparation of glycidyl silicon ethers by reaction of glycidol with chlorosilanes in the presence of a hydrogen chloride acceptor (*e.g.*, triethylamine). About the same time, Andrianov and Dubrovina[2] reported the synthesis of alkylacetoxyepoxysilanes; and Brynolf[3] prepared 3,4-epoxybutyltrimethylsilane by the reaction of trimethylsilylmethylmagnesium bromide with epichlorohydrin followed by treatment with base. Very recently, Plueddemann and Fanger[4] reported an interesting series of epoxyorganosiloxanes formed either by peracetic acid epoxidation of olefinic organosilicon compounds, or by addition of silicon hydrides across the olefinic bond of unsaturated epoxy compounds.

Evidently silicon analogs of commercial epoxy (Epon) resins have not been described. In this paper we wish to report the synthesis of 4-(2,3-epoxypropoxy)phenyltrimethylsilane, IV, a silicon analog of the well known phenyl glycidyl ether.[5,6]

This new type of epoxysilane was synthesized using the following sequence of reactions:



Compounds I, II, and III have been reported previously,[7–10] although modifications of the published procedures were employed in the present work. Reaction of 4-trimethylsilylphenol (III) with epichlorohydrin in basic solution at room temperature (20°) was found to proceed readily, the optimum yield of IV being obtained at about a 1:3 molar ratio of III with epichlorohydrin. The use of less epichlorohydrin resulted in the formation of larger amounts of the secondary product, 1,3-bis(4-trimethylsilylphenoxy)-2-propanol, V, by reaction of IV with III.

EXPERIMENTAL

4-Bromophenoxytrimethylsilane. I. A mixture of 4-bromophenol (865 g., 5.0 moles), anhydrous benzene (900 ml.), and pyridine (395 g., 5.0 moles) was cooled in an ice bath at 0–5°; then trimethylchlorosilane (542.5 g., 5.0 moles) in benzene (500 ml.) was added dropwise with stirring. Throughout the addition care was taken to maintain the temperature in the range 5–20°. After stirring for 3 hr., and standing overnight, the precipitated pyridinium chloride was filtered. The filtrate was distilled at atmospheric pressure to remove most of the benzene, and the residue was distilled *in vacuo*, the fraction of b.p. 120–130°/20–30 mm. being collected. Refractionation gave pure I of b.p. 122°/20 mm., in good agreement with the literature value.[7,9] The yield was 882 g. (72%).

It should be noted that specimens of this compound partially decomposed to 4-bromophenol on standing for several weeks in tightly-stoppered Pyrex glass bottles. The infrared spectrum of freshly prepared I showed no bands due to hydroxyl. These developed gradually and it was considered inadvisable to use specimens of I older than about 1 month for Grignard syntheses.

4-Trimethylsilylphenoxytrimethylsilane. II. A modification of the synthesis of Frisch and Shroff[9] was employed using tetrahydrofuran rather than ether as solvent. This was

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