with ice, and the mixture was acidified with hydrochloric acid. The aqueous layer containing the amine hydrochloride was washed with several portions of ether and then treated as described below.

Isolation of the hydrochloride of 2,3-diphenyl-1-aminopropane (27) from its water solution proceeded by removing all volatiles. The drying was completed by repeated azeotropic distillations with benzene. The product was extracted by boiling the dry mixture with 100 mL of chloroform for 5 min. The filtered chloroform solution was stripped of solvent, and the residue was crystallized from concentrated hydrochloric acid (12 mL). The resulting white neeldes of 2,3-diphenyl-1-aminopropane hydrochloride showed a melting point of 187–188 °C (lit.[16] mp 188–190 °C).

Anal. Calcd for $C_{15}H_{18}ClN$: C, 72.72; H, 7.27. Found: C, 72.38; H, 7.21.

The yield of hydrochloride **27** as obtained directly from cinnamonitrile **26** was 8%; the yield via the oxime was 31%.

Stirring the hydrochloride (1.2 g, 5.0 mmol) of 2,3-diphenyl-1-aminopropane (**27**) with benzenesulfonyl chloride (1.2 g, 7.0 mmol) and excess 5% aqueous sodium hydroxide for 10 h at room temperature afforded the corresponding sulfonamide. Two crystallizations from methanol gave white crystals (1.0 g, 61%) of 2,3-diphenyl-1-benzenesulfonamidopropane (**29**, mp 94–98 °C) which was homogeneous according to TLC.

Anal. Calcd for $C_{21}H_{21}NO_2S$: C, 71.70; H, 5.98. Found: C, 71.62; H, 5.97.

Exposure of Test Compounds to the Action of Aluminum Chloride in Benzene. All the experiments were performed by following the same general procedure as described above for the reaction with radioactive 1-benzenesulfonyl-2-(bromomethyl)-ethylenimine (**1**). The molar ratio of substrate to catalyst was held close to 1.5:1, and the amount of benzene corresponded to 3.8–4.4 mL/mmol of substrate. The 3,3-diphenyl-1-benzenesulfonamidopropane product was routinely characterized by its melting point and mixture melting point as well as by comparison of the proton magnetic resonance and infrared absorption curves. Thin-layer chromatography was frequently employed. The yield from the several test compounds as given in Table I should be compared to the 20–30% yields of 3,3-diphenyl-1-benzenesulfonamidopropane obtained from 1-benzenesulfonyl-2-(bromomethyl)ethylenimine.

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Registry No. **1**, 78515-28-3; **3**, 78515-29-4; **4**, 78515-30-7; **5**, 78515-31-8; **6**, 78515-32-9; **7**, 78515-33-0; **8**, 78515-34-1; **9**, 78515-35-2; **10**, 119-61-9; **10** semicarbazone, 14066-73-0; **12**, 34541-67-8; **13**, 78529-86-9; **14**, 78515-36-3; **15**, 78515-37-4; **16**, 78515-38-5; **18**, 15028-44-1; **19**, 1795-98-8; **20**, 78515-39-6; **21**, 50411-26-2; **22**, 78515-40-9; **23**, 78515-41-0; **24**, 62247-39-6; **25**, 78515-42-1; **26**, 2510-95-4; **27**·HCl, 40692-28-2; **28**, 2016-03-7; **28** oxime, 78515-43-2; **29**, 78515-44-3; paraformaldehyde, 50-00-0; 1,3-bis(benzenesulfonyloxy)-2-benzenesulfonamidopropane-2-^{14}C, 78515-45-4; benzenesulfonyl chloride, 98-09-9; bromobenzene, 108-86-1; benzoic acid, 65-85-0; 2-benzylethylene oxide, 4436-24-2; ethyl α-phenylcyanoacetate, 4553-07-5; benzenesulfonyl-2-(bromomethyl)ethylenimine, 5120-12-7.

Notes

Kinetic Acetonation of Sucrose: Preparative Access to a Chirally Substituted 1,3,6-Trioxacyclooctane System[1]

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Acetonation (O-isopropylidenation) of sugars and their derivatives constitutes one of the most widely used modes for the protection of selected diol groups in sugar-based syntheses.[2] The conventional method for the preparation of such acetals employs acid catalysis under conditions wherein thermodynamic control prevails. Numerous mono- and polyisopropylidene acetals of monosaccharide sugars find application as routine intermediates in synthesis,[2,3] and the general factors that determine the structures of the favored products, through competition between the various available hydroxyl groups and different tautomeric forms of the sugar, are well understood.[4] Nevertheless, the standard preparative conditions, usually employing acetone in excess as the solvent, plus an acid catalyst, generally in the presence of anhydrous copper(II) sulfate, limit the accessible products to those preponderant at thermodynamic equilibrium. Acid-labile bonds in the carbohydrate derivative are broken during the reaction. Thus, the acetonation of sucrose (β-D-fructofuranosyl α-D-glucopyranoside, **1**)[5] under standard conditions leads solely to the normal products of acetonation of the constituent monosaccharides,[6] namely, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**2**) and 1,2:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**3**); the acid-sensitive acetal bond of the disaccharide is broken, and the ring size of each sugar component is changed.

A method for acetonation of sugars developed in one of our laboratories[7-10] allows the introduction of *O*-isopropylidene groups under exclusively kinetic conditions

(1) Supported, in part, by RCP 529 of the CNRS, and NIH Grant GM-11976.

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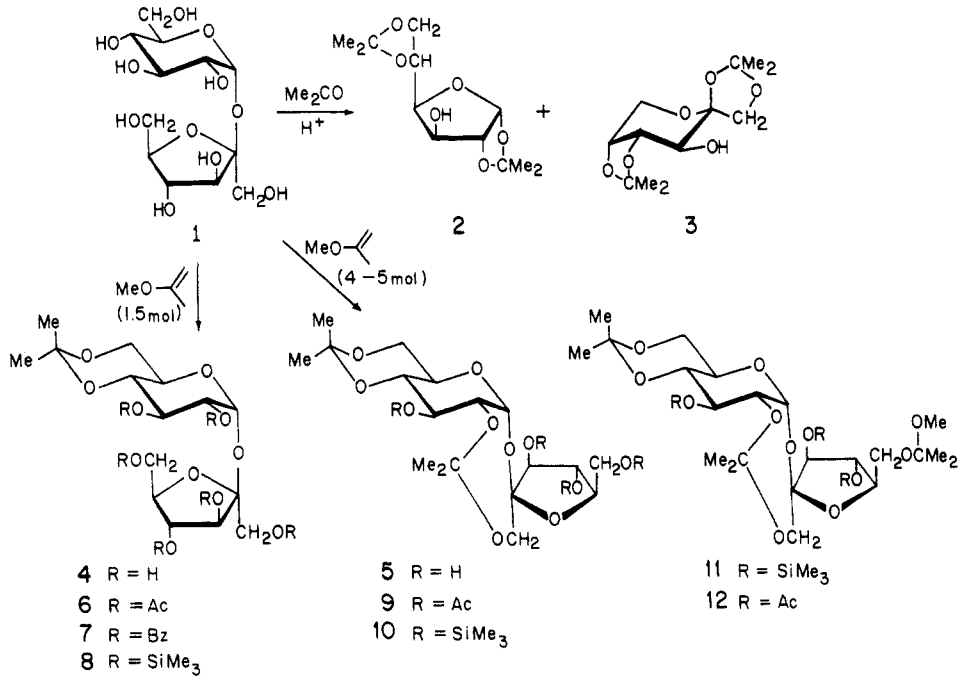
0022-3263/81/1946-4057$01.25/0

Scheme I



and permits access to an entirely different range of protected sugar derivatives, which serve to complement those obtainable by the traditional, thermodynamic route. The procedure, which employs a controlled amount of 2-alkoxypropene as the reagent, a solvent (*N*,*N*-dimethylformamide) compatible with both the sugar and the reagent, a desiccant, and a trace of *p*-toluenesulfonic acid, has been systematically evaluated with aldopentoses,[8] aldohexoses,[9] and ketohexoses.[10] It is shown[7-11] that these kinetic products are formed without cleavage of acid-sensitive bonds and without tautomerization of the sugar at the acetonation step and that the anomeric center of the sugar is not a favored site of reaction. The procedure has important potential for the synthesis of complex saccharides such as those which occur in specific biological determinants, especially inasmuch as the normal (pyranoid) ring form of the sugar is retained and the anomeric (hemiacetal) center is left unsubstituted and thus accessible for glycosidic coupling reactions.

High yields of kinetic acetal products are achieved by use of 2-alkoxypropenes, provided that the medium is kept scrupulously dry and only a trace of acid catalyst is used; an excessive amount of acid leads to lowered yields and difficultly separable mixtures containing both kinetic and thermodynamic products. 2,2-Dimethoxypropane has been used as an acetonating reagent, and products of kinetic acetonation have been isolated,[12-15] but the yields are generally low and complex chromatographic purification is required to separate the product mixtures, as these generally result from a mixed-mode kinetic–thermodynamic acetonation.

Optimal conditions for kinetic acetonation with 2-alkoxypropenes may be conveniently established by small-scale experiments monitored by GLC of trimethysilylated aliquots. Following such a determination of optimal conditions for conversion into a single product, the acetonation may then be repeated, but with acetylation of the acetonated derivative, isolation of the acetylated product, and structural characterization by physical and chemical methods.

The great abundance of sucrose renders it a potentially attractive starting point for organic synthesis, although few nonfood uses for this ubiquitous plant food reserve have been found thus far. It is estimated that less than 1% of the world production ($\sim 10^8$ tons per annum) of this pure organic chemical is employed in nonfood uses.[16] This report describes the preparative-scale conversion of sucrose, by the action of 2-methoxypropene, into its 4,6-monoisopropylidene acetal (**4**) and its 2,1′:4,6-diisopropylidene acetal (**5**; see Scheme I); the latter contains an unusual 1,3,6-trioxacyclooctane ring, and both acetals constitute potentially useful starting materials in organic synthesis.[13,15,17,18]

For exploratory experiments, solutions of sucrose (**1**) in *N*,*N*-dimethylformamide containing Drierite were allowed to react at 0–5 °C with various molar proportions of 2-methoxypropene in the presence of a trace of *p*-toluenesulfonic acid, and aliquots of the mixture were examined by GLC after trimethylsilylation. With 2 equiv of the reagent, a silylated monoacetal (shown to be the 4,6-acetal derivative **8**) was the major product, together with small proportions of apparent diacetal derivative **10** and some of the octakis(trimethylsilyl) ether of sucrose, whereas use of 4–6 mol of reagent gave mostly the diacetal derivative **10**, negligible amounts of monoacetal and unreacted sucrose derivatives, and a small amount of product considered (mass spectrum) to be the per(trimethylsilyl) ether (**11**) of the diacetal **5**, further substituted by an acyclic acetal group on O-6′.

Repetition of the experiments under the conditions giving maximal conversion into the monoacetal and diacetal, respectively, but with subsequent acetylation of the

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(12) Hasegawa, A.; Fletcher, H. G., Jr. *Carbohydr. Res.* **1973**, *29*, 209–222.
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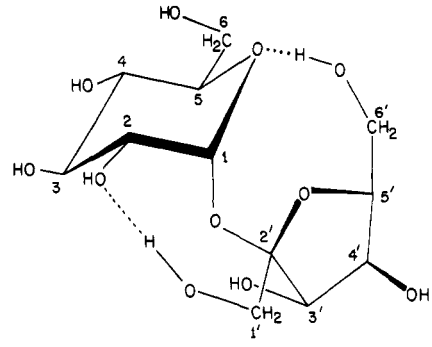
reaction mixtures and separation by TLC on silica gel, gave pure products that were examined by ^1H NMR spectroscopy. The products were not indefinitely stable in contact with silica gel, and separations were completed without undue delay. The reaction employing a 2 molar excess of 2-methoxypropene gave a major (62%) product identified as the acetylated monoacetal **6** from its NMR spectrum and by reference to a sample previously characterized[15] that had been isolated chromatographically after acetonation of sucrose with 2,2-dimethoxypropane. Accompanying **6** in the product was ~5% of sucrose octaacetate and ~5% of the acetylated diacetal **9**.

Acetonation with 4 mol of 2-methoxypropene, followed by acetylation and TLC resolution, gave a mixture containing a negligible proportion (~1%) of sucrose octaacetate. The major (~60%) product was the acetylated diacetal **9**, which was isolated crystalline and whose ^1H NMR spectrum indicated it to be the acetylated 2,1′:4,6-diacetyl derivative identical with a low-yield product[13,14] isolated later[19] in 38% yield from a mixture obtained by treating sucrose with 2,2-dimethoxypropane and *p*-toluenesulfonic acid. The structure attributed to **9** from analysis of its ^1H NMR spectrum is unequivocally affirmed from the result of an X-ray crystal structure determination.[19] A third, minor (~1%) component in the 4 M acetonation product, migrating in TLC more rapidly than **9**, was assigned from its NMR spectrum and other properties as the triacetal derivative **12**; it was very acid labile, as would be anticipated from the presence of the acyclic acetal group. The proportion of this component rose to ~10% when 6 mol of acetonating reagent was used.

Emphasis was then placed on establishing convenient, preparative conditions for the large-scale, one-flask conversion of **1** into the diacetal **5** without recourse to chromatographic procedures during product isolation. Optimal conditions for the preparation employed sucrose in *N,N*-dimethylformamide containing molecular sieves treated with a 5 molar excess of 2-methoxypropene and a strictly catalytic amount of *p*-toluenesulfonic acid for 40 min at 70 °C. Subsequent treatment with acetic anhydride and pyridine, followed by evaporation of all reagents, gave the crystalline tetraacetate (**9**) of the diacetal **5** in 70% yield.

For preparative access to the monoacetal **4**, a 1.3 molar excess of 2-methoxypropene was used, and the reaction was conducted for 40 min at 70 °C. Isolation of pure **4** was best accomplished by passage of the product through a column of silica gel to remove a small proportion (~7%) of the diacetal **5** (which was eluted first) and give the second, major band of monoacetal **4** as a white solid in 60% yield, further characterized as its hexaacetate **6** and crystalline hexabenzoate **7**.

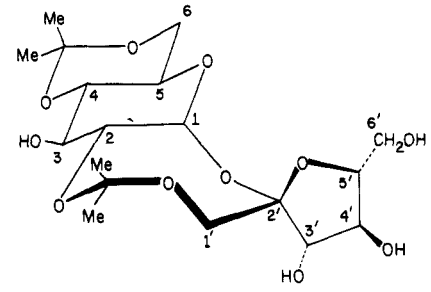
The course of the reaction leading from **1** to **4** and **5** may be readily rationalized in the light of (a) general principles advanced[8,9] for interpreting the acetonation reaction of sugars with 2-alkoxypropenes under kinetic control and (b) the established geometry of the sucrose molecule. Sucrose (**1**) has been the subject of an extremely accurate crystal structure analysis by neutron diffraction,[20] and the conformation of the molecule is shown (**1a**) to be stabilized by two hydrogen bonds, between HO-1′ and O-2 and between HO-6′ and O-5. Initial attack by the reagent at O-6, the most sterically available of the three primary hydroxyl groups, to yield a transitory ion of the type $C(6)H_2O{=}CMe_2^+$ or an acyclic acetal $C(6)H_2OCMe_2OMe$, would



1a

proceed rapidly because of unhindered access to O-4 to generate the 1,3-dioxolane ring, which would be quite stable under the conditions of reaction and lead to accumulation of the product **4**.

A greater excess of the reagent would then predictably initiate attack at one of the other primary positions (O-1′ or O-6′). Reaction at O-1′ would permit direct bridging to O-2 to generate the observed diacetal **5** with minimal displacement from the favored geometry of sucrose (**1a**) dictated by hydrogen bonds, as the 2,1′-*O*-isopropylidene group can be accommodated with little perturbation of the relative orientation of the rings in and substituents on the sucrose molecule. This aspect may be visualized in a conformational representation (**5a**) of the diacetal **5**. In



5a

contrast, the generation of other cyclic acetals involving O-1′ would be either sterically impossible (3,1′) or strained (1′,3′ or 1′,6′) or would require rotation to an unfavored orientation (1′,4′). Likewise, attack by the reagent at O-6′ cannot be followed by direct cyclization with a proximal hydroxyl group; rotation to other orientations would be required (2,6′ or 3′,6′) or would lead to significant, or intolerable, steric clashes (3,6′) or ring strain (1′,6′ and 4′,6′).

Following formation of the diacetal **5**, forcing conditions with an excess of the reagent led to substitution at O-6′, but there was no indication to suggest that the resultant, acyclic 6′-acetal (examined as its derivatives **11** and **12**), underwent conversion into a stable, cyclic form, even though a 3′,6′-acetal bridge would appear sterically feasible. The observed products (**11** and **12**) displayed the high acid lability anticipated for such noncyclized acetals, and they decomposed on storage or even on prolonged exposure to silica gel.

The correlation observed here between the favored conformation of the disaccharide **1** and the structure of the diacetal **5** suggests that kinetic acetonation of oligosaccharides may prove valuable as a tool for probing interresidue conformations of oligosaccharides, and such investigations could be of particular utility for noncrystalline materials. In the reverse sense, crystallographically determined structures may provide a useful basis for predicting the outcome of kinetic-acetonation reactions and for permitting the design of unusual, polyoxygenated, large

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Table I

	yield, %			
expt	12	9	6	sucrose octaacetate
A		3-5	62	5-6
B	trace	50-55	20	1-2
C	7-10	45-50	3-5	trace

rings of interest as specific metal ion complexants or chiral, synthetic intermediates.

Diacetal **5** has the eight-membered ring in a boat–chair conformation (**5a**) and possesses eight chiral centers. Its ready accessibility at low cost suggests that it may have significant potential as a precursor for synthesis.

Experimental Section

Evaporations were performed under diminished pressure. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter in 1-dm tubes. Column chromatography was performed with Kieselgel (Merck, 70–230 mesh) and TLC with silica gel 60 F-254 (Merck), with detection by charring with sulfuric acid.

Analytical Evaluation of the Acetonation of Sucrose with 2-Methoxypropene. Solutions of sucrose (2.5 g) in dry *N,N*-dimethylformamide (150 mL) containing ~10 mg of *p*-toluenesulfonic acid and Drierite (1 g) were stirred at 0–5 °C with the addition of 2 molar equiv of 2-methoxypropene. After 2 h of reaction, one experiment (A) was terminated, and to two remaining experiments (B and C) was added a further 2 molar equiv of 2-methoxypropene, and stirring was continued for a further 2 h, whereupon the second experiment (B) was terminated. An additional 2 molar equiv of 2-methoxypropene was added to the remaining experiment (C), and the reaction was terminated after a further 2 h of stirring of 0–5 °C.

Aliquots of the terminated reaction mixtures were per(trimethysilylated) with Tri-Sil Z (Pierce Chemical Co.), the products were analyzed by GLC in a column of OV-1 (2%) operated at 220 °C, and the observed peaks were compared with those given by reference samples of octakis(trimethysilyl)sucrose, the hexakis(trimethylsilyl) ether (**8**) of 4,6-*O*-isopropylidenesucrose (**4**), and the tetrakis(trimethylsilyl) ether (**10**) of 2,1′:4,6-di-*O*-isopropylidenesucrose (**5**), whose retention times were in the order **10** > **8** > octakis(trimethylsilyl)sucrose. Experiment A showed three peaks, the major one (~70%) corresponding to **8** and the minor ones (~15% each) to **10** and octakis(trimethylsilyl)sucrose. The peak for **10** was preponderant (~70%) in experiment B, about 20% of **8** was present, and the sucrose ether was very minor. A minor, fast-migrating peak was also observed. The diacetal derivative **10** was the principal product (~80%) in experiment C. Peaks for **8** and octakis(trimethylsilyl)sucrose were negligible, but the fast-moving peak, eluted before **10**, had increased to ~15%; this component was considered to be 2,1′:4,6-di-*O*-isopropylidene-6′-*O*-(1-methyl-1-methoxyethyl)-2,2′,3′-tri-*O*-(trimethylsilyl)sucrose (**11**) from further evidence described next.

Each of the reactions (A–C) was terminated by addition of anhydrous sodium carbonate (~3 g) and stirring for 1 h at 0 °C. The mixtures were filtered, the filtrates evaporated, and the residues acetylated with acetic anhydride–pyridine. The acetylated product mixtures were resolved by column chromatography on silica gel with ethyl acetate–petroleum ether (bp 40–65 °C) mixtures as the eluant. (Some decomposition of the products was observed when contact with the silica gel was prolonged, and this could be retarded by inclusion of a few drops of trimethylamine in the eluant.)

Four separate compounds were isolated pure from the chromatographic separations. In the order of increasing elution times, these were 3,2′,3′-tri-*O*-acetyl-2,1′:4,6-di-*O*-isopropylidene-6′-*O*-(1-methyl-1-methoxyethyl)sucrose (**12**), the diacetal tetraacetate **9**, the monoacetal hexaacetate **6**, and sucrose octaacetate. The last three compounds were each identified by direct comparison with the known reference compounds and gave ^{1}H NMR spectra free from extraneous peaks and identical with those of authentic samples. The isolated yields of the four products in the three experiments were as shown in Table I.

The ^{1}H NMR spectrum of **12** (in $CDCl_3$, C_6D_6, and Me_2CO-d_6) showed the following principal signals: δ 1.2–1.5 (18 H, $3CMe_2$), 2.0–2.2 (9 H, 3 peaks, 3OAc), 3.2 (3 H, OMe), 3.4–4.4 (m, 10 H), 5.2 (d, 1 H, $J_{3',4'}$ = 6.5 Hz, H-3′), 5.3 (apparent t, 1 H, $J_{2,3} \approx J_{3,4} \approx 9$ Hz, H-3), 5.6 (dd, 1 H, $J_{3',4'}$ and $J_{4',5'}$, 6.5 and 4.8 Hz, H-4′), 6.2 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1).

Compound **12** was a syrup that was not very stable; after some weeks of storage at 0 °C, its NMR spectrum showed evidence of substantial decomposition.

Preparative Conversion of Sucrose (1) into 3,3′,4′,6′-Tetra-*O*-acetyl-2,1′:4,6-di-*O*-isopropylidenesucrose (9). A solution of sucrose (34.2 g, 0.1 mol) in dry *N,N*-dimethylformamide (400 mL) containing molecular sieve pellets ($^1/_{16}$ in., Type 3 A) was stirred with 2-methoxypropene (60.5 mL, 0.5 mol) in the presence of *p*-toluenesulfonic acid (25 mg) for 40 min at 70 °C. The mixture was cooled to room temperature and then treated with acetic anhydride (150 mL) and pyridine (400 mL) for 24 h at room temperature. TLC (6:1 ether–petroleum ether) showed a fast-moving, major product. The solution was evaporated, with addition of toluene during evaporation, to give a syrup that crystallized from ether–petroleum ether to give **9**: yield 46.5 g (70%); mp and mmp 136–137 °C; $[\alpha]_D$ +13° (*c* 1, chloroform). The physical constants and ^{1}H NMR spectrum of **9** were identical with those of an authentic sample.[13,17]

Preparative Conversion of Sucrose (1) into 4,6-*O*-Isopropylidenesucrose (4). A solution of sucrose (34.2 g, 0.1 mol) in dry *N,N*-dimethylformamide (400 mL) containing molecular sieve pellets ($^1/_{16}$ in., Type 3 A) was stirred with 2-methoxypropene (12.1 mL, 0.13 mol) in the presence of dry *p*-toluenesulfonic acid (25 mg) for 40 min at 70 °C, cooled to room temperature, and made neutral with anhydrous sodium carbonate. The inorganic residue was filtered off and the filtrate evaporated to a syrup. Elution of the syrup from a column of silica gel with 1:1 ethyl acetate–acetone afforded the diacetal **5** as a syrup: 3 g (7%); $[\alpha]_D$ +25.5° (*c* 1, methanol). Further elution gave the major product **4**: yield 23 g (60%); white powder; $[\alpha]_D$ +45.4° (*c* 1, methanol).

Treatment of **4** (1 g) with acetic anhydride (4 mL) in pyridine (10 mL) gave 2,3,1′,3′,4′,6′-hexa-*O*-acetyl-4,6-*O*-isopropylidenesucrose (**6**): 1.82 g (94%); $[\alpha]_D$ +45.4° (*c* 1, chloroform) [lit.[15] $[\alpha]_D$ +46.0° (*c* 0.2 chloroform). The ^{1}H NMR and mass spectra of **6** were identical with those of an authentic sample.[15]

Conventional benzoylation of **4** with benzoyl chloride in pyridine gave the crystalline 2,3,1′,3′,4′,6′-hexa-*O*-benzoyl-4,6-*O*-isopropylidenesucrose (**7**): mp 170–172 °C (from ethanol); $[\alpha]_D$ +47.2° (*c* 1, chloroform) [lit.[15] mp 168–170 °C; $[\alpha]_D$ +46.0° (*c* 1, chloroform)]. The ^{1}H NMR and mass spectra were identical with those of an authentic sample.[15]

Acetylation of the solid diacetal **5** with acetic anhydride–pyridine gave the known,[13,17] crystalline 3,3′,4′,6′-tetra-*O*-acetyl-2,1′:4,6-di-*O*-isopropylidenesucrose (**9**), mp and mmp 136–137 °C (from ether–petroleum ether).

Registry No. **1**, 57-50-1; **4**, 71196-27-5; **5**, 67909-39-1; **6**, 60825-18-5; **7**, 60825-19-6; **8**, 78479-74-0; **9**, 57471-93-9; **10**, 78479-75-1; **11**, 78498-50-7; **12**, 78479-76-2; 2-methoxypropene, 116-11-0; octakis(trimethylsilyl)sucrose, 19159-25-2; sucrose octaacetate, 126-14-7.

Peri-Bridged Naphthalenes. 5. Improved Synthesis of 1-Thiaphenalene

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We had been interested in the synthesis of aromatic chalcogen-containing organic compounds such as **1** and its selenium and tellurium analogues because of their possible incorporation into "one-dimensional" solids.[1] This interest

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