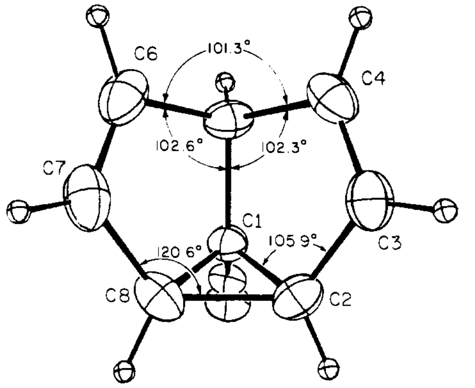

Figure 2.

C(4) and C(6) at approximately right angles to one another. A direct comparison of these data with the structural features of semibullvalene in the gas phase as determined by electron-diffraction methods[23] is informative. Further exploration of this chemistry as a method for introducing more varied substituents is in progress.[24]

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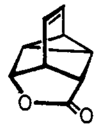
(14) ^{1}H NMR (CDCl$_3$) δ 6.54 (m, $J_{7,8}$ = 6, $J_{8,9}$ = 8 Hz, H$_8$), 5.80 (t of d, $J_{9,10}$ = 8, $J_{7,9}$ = 2 Hz, H$_9$), 4.78 (m, $J_{1,6}$ = $J_{1,10}$ = 2 Hz, H$_1$), 3.22 (br d, H$_{10}$), 3.03 (br s, H$_4$), 2.53 (tr of d, $J_{5,7}$ = $J_{6,7}$ = 5.5 Hz, H$_7$), and 1.85–2.38 (overlapping t, H$_5$ and H$_6$); ν_{max} (CHCl$_3$) 1722 cm^{-1}.

(15) Reductive dechlorosulfonylation of this mixture affords in addition to the parent lactam derived from **2**, lactone i of related structure and the 2 + 2 cycloadduct ii in minor amounts.



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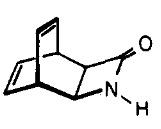

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(17) ^{1}H NMR (CDCl$_3$) δ 6.64 (q, $J_{1,7}$ = 3, $J_{6,7}$ = 5.5 Hz, H$_7$), 6.26 (m, $J_{1,2}$ = 6, $J_{2,3}$ = 9.5, $J_{2,4}$ = 2 Hz, H$_2$), 5.93 (q, $J_{5,6}$ = 3 Hz, H$_6$), 5.43 (m, $J_{3,4}$ = 2, $J_{3,5}$ = 1 Hz, H$_3$), 4.41 (m, $J_{4,5}$ = 3 Hz, H$_4$), 3.38 (s, H$_8$), 3.32 (m, H$_5$), and 3.10 (m, H$_1$).

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(20) Solvent and inductive effects have necessarily been disregarded. However, because the cyano function is positioned δ to C$_4$,C$_8$, through-bond effects are expected to be minimal. The Hoffmann–Stohrer prediction has **4a** stabilized by 0.37 eV.[8]

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(24) We acknowledge partial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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A New Synthesis of Sucrose Which Demonstrates a Novel Approach to the Synthesis of α-Linked Disaccharides[1]

Sir:

In spite of recent advances[2] in the field, stereochemically controlled preparation of α-linked disaccharides remains one of the most challenging frontiers in synthetic organic chemistry.[3] Among compounds linked in this manner are some of the most important biologically, pharmacologically, and clinically active substances, and frequently the structural features of the individual saccharide components vary widely.[4] We describe herein a novel approach to the synthesis of α-linked disaccharides which is capable of accomodating a wide variety of structural modifications, and, as a case in point, we illustrate this potential by outlining a synthesis of sucrose[5] from known starting materials.

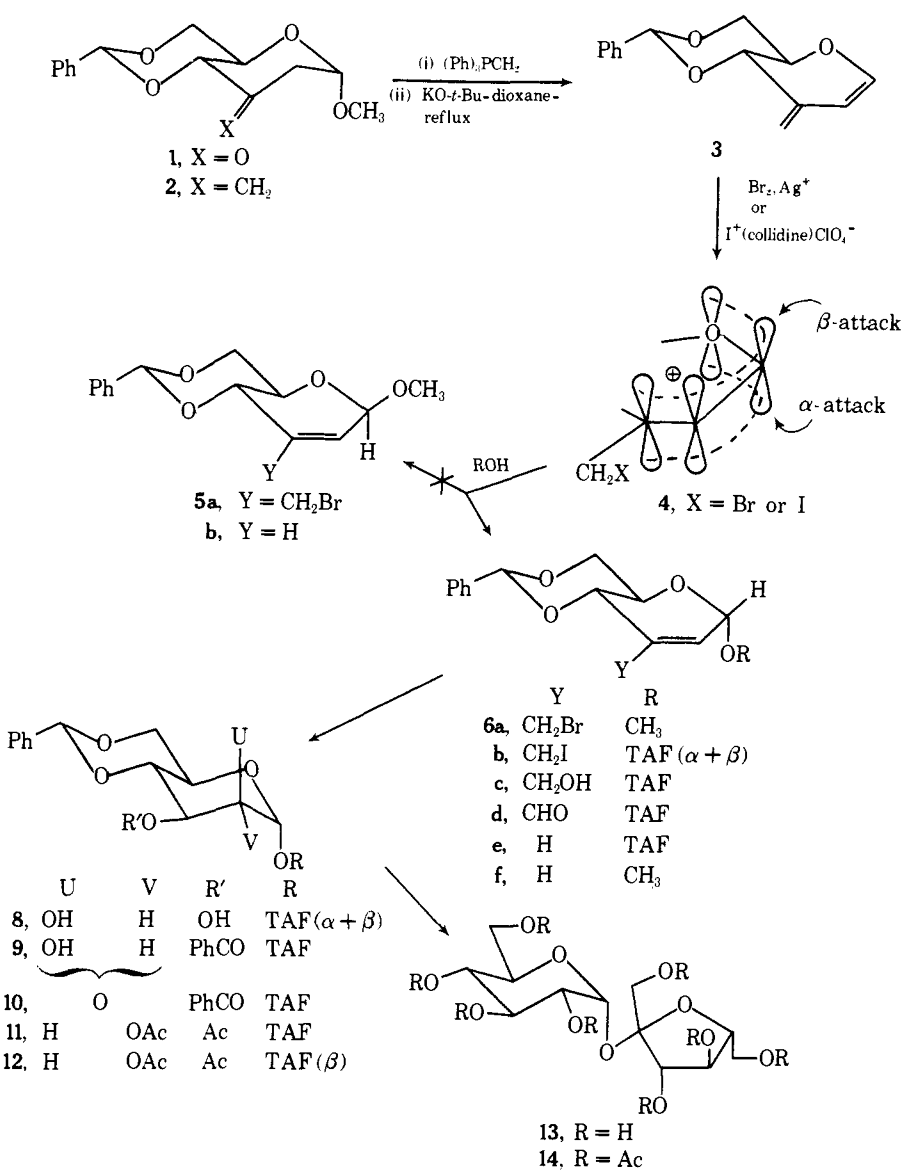
Specifically, (i) the disaccharide linkage is forged by the agency of an electrophile, a novel development which might be availing where current nucleophilic–solvolytic type condensations[2,7] are inapplicable; (ii) the glucosyl moiety is elaborated from an hex-2-enopyranoside, a type of unsaturated sugars of demonstrated versatility in monosaccharide modification;[8,9] (iii) congeners of some of the intermediates, e.g., **16** have provided access to 2-amino-2-deoxydisaccharides of pharmacological importance;[10] (iv) the linkage of the fructosyl unit via a tertiary alcohol (actually a tertiary ketol) occurs in 45% yield; (v) all steps in the synthesis occur under mild conditions and are so stereo- or regiospecific that no chromatographic fractionations are necessary, excepting that following the initial condensation.

The key to the synthesis reported here is diene **3**,[11] prepared most expeditiously by elimination of methanol from **2**,[12] the latter being obtained from ketone **1**.[13] Diene **3** has been shown to undergo methoxybromination to the α-glycoside **6a**,[14] a result which may be rationalized in terms of the extensively delocalized allyloxocarbonium ion, **4**, resulting from electrophilic attack on **3** (Scheme I). Ion **4** is expected to capture the nucleophile preferentially on the α-face since the product so formed (**6a**) allows for better continuous overlap with the intermediate than does the alternative β-product (**5a**). Interestingly, in analogy with the "axial haloketone" principle,[15] compound **6a** would not only be the kinetic product but is thermodynamically favored because of the Edward–Lemieux effect.[16]

The foregoing advantage, based on an electronic assessment, is complemented by an equally favorable stereochemical prognosis. Thus intermediate **4**, because of its planar foreground, presents no steric obstacles to the approaching nucleophile.

Condensation of diene **3** and tetraacetylfructofuranose **7** under the agency of iodonium ion[17] afforded compound **6b**

Scheme I

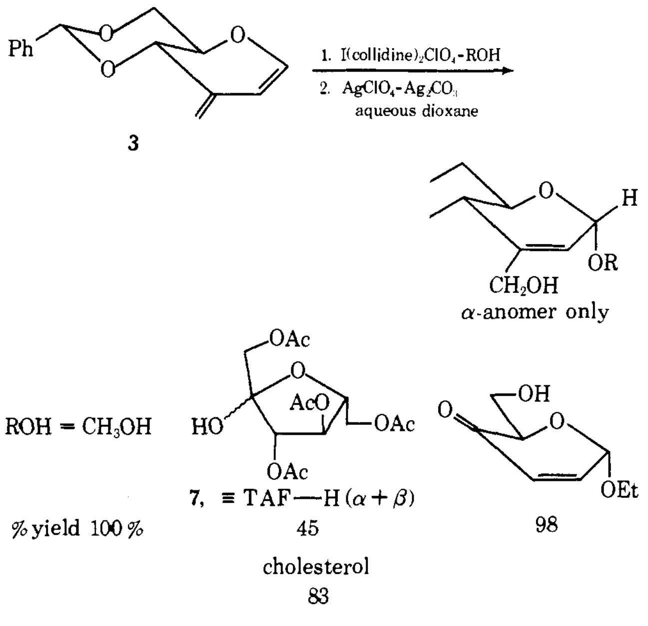


as *the only substance representing a union of 3 and 1.*[20] Compound **6b** was converted to **6d**[23] either directly using $AgBF_4$-DMSO-Et_3N oxidation[24] (80%), or indirectly by hydrolysis (Ag^+-aqueous dioxane) to alcohol **6c**[23] (98%) followed by oxidation (71%). Aldehyde **6d** was decarbonylated to the olefin **6e**[23] (79%) using Wilkinson's reagent.[25]

In keeping with previous studies on compound **6f,** hydroxylation[26] of **6e** with OsO_4 in pyridine gave only the manno diol **8** (84%). The problem of inverting the configuration at carbon-2 was solved by taking advantage of the greater reactivity of the equatorial alcohol toward acylation.[27] Thus benzoylation of **8** at −30° in pyridine–methylene chloride solution gave **9** exclusively (75%), which was oxidized with $CrO_3{\cdot}2C_5H_5N$ in methylene chloride to the keto benzoate **10** (80%). The latter was treated with excess $NaBH_4$ in methanol[28] and the product directly acetylated to give **11** (87%).

4,6-*O*-Benzylidenehexaacetylsucrose, **12,** has recently been synthesized,[29] and comparison of the 220-MHz spectra of **12** with the synthetic preparation confirmed the presence of the sucrosyl skeleton in the mixture, **11.** Nucleation with an authentic sample of **12** kindly supplied by Dr. Khan afforded the desired material: mp 162–164°; mmp. 161.5–

Scheme II



163°; authentic sample 162.5-164.[30] Since **12** can be debenzylidenated and converted to sucrose **13** or its octaacetate **14**, the foregoing constitutes a total synthesis of sucrose.

The promise of dienoid receptors for the synthesis of divers α-linked di- and oligosaccharides is apparent from the results in Scheme 2 where a range of alcohols and the yields obtained are reported. Notably only α-D anomers have been observed. Sample syntheses designed to develop this approach are underway and will be reported in due course.

Acknowledgments. We are indebted to Professor J. K. Saunders of the University of Sherbrooke for recording and interpreting the ^{13}C NMR spectra and to Dr. R. Khan of Tate and Lyle, Reading, U.K., for a sample of compound **12**.

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(17) Iodonium dicollidine perchlorate[18] (620 mg, 1.31 mmol) was added over a period of 20 min to a benzene (20 ml) solution containing diene **3** (200 mg, 0.870 mmol) and tetraacetylfructofuranose[19] **7** (1.51 g, 4.35 mmol) the latter having been dried previously by azeotropic distillation with benzene. TLC monitors indicated that reaction was immediate, and there was a product, **6b**, R_f 0.48 (ethyl acetate-petroleum either 30-60°) which was isolated in 45% yield (272 mg) by column chromatography on silica gel.

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(30) These values are uncorrected.

(31) Holder of a National Research Council of Canada Studentship, 1973-1975.

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Reversibility in the Formation of Stoichiometric Surface Molybdenum Carbonyls on Alumina

Sir:

Suitable activation converts molybdenum hexacarbonyl adsorbed on γ-Al_2O_3 into a catalyst for the metathesis of olefins at low temperatures.[1,2] Sweeping $Mo(CO)_6/\gamma$-Al_2O_3 with a flow of ultrapure helium at 100° results in the loss of carbon monoxide and the formation of a material with catalytic activity and an empirical composition of $Mo(CO)_3$ads. Preliminary data indicated that decomposition terminated very approximately at $Mo(CO)_5$ads when the treatment was in a closed vessel with resulting development of a partial pressure of carbon monoxide, and that exposure of $Mo(CO)_3$ads to carbon monoxide at −17° converted it to $Mo(CO)_4$ads.[3] Further data support the existence of this novel group of stoichiometric surface compounds and establish that the formation of these compounds can be reversed to molybdenum hexacarbonyl plus γ-Al_2O_3 by appropriate treatment with carbon monoxide with proportional loss in catalytic activity. Our data are summarized in Figure 1.

$Mo(CO)_3$ads was prepared by cleaning 0.250 g of 60-80 mesh γ-Al_2O_3 (Harshaw Chemical Co. AL3940, prepared from Catapal SB) in flowing oxygen at 450°, cooling in helium, impregnating at 0° with a pentane solution of $Mo(CO)_6$ (to provide about 15 mg $Mo(CO)_6$/g Al_2O_3 in most experiments), evaporating the pentane in a flow of helium at 0°, and then activating for 1 hr at 100° in a flow of helium. The evolved carbon monoxide was trapped at −196° on wide pore silica gel (Davison grade 62) and later released by warming for catharometric measurement.[3,4] In these experiments, 3.00 ± 0.03 CO/Mo were released. In the absence of alumina, decomposition is very slow at 100°.

A helium sweep of the reactor after heating $Mo(CO)_6/Al_2O_3$ in a closed system at 100° for 1 hr followed by cooling to 0° collected 1.02 CO/Mo. The P_{CO} at the end of the activation at 100° was about 0.07 atm.

A reactor containing $Mo(CO)_3$ads was exposed to 1 atm of carbon monoxide for 30 min at 100°, cooled to −17° evacuated, and purged with helium for 15 min. Reconversion of the resulting material to $Mo(CO)_3$ads by a helium sweep at 100° for 50 min liberated 2.12 ± 0.14 CO/Mo (three experiments).

During the passage of several pulses of carbon monoxide in a helium carrier over $Mo(CO)_3$ads at −16°, 1.06 CO/Mo disappeared. In seven other experiments, $Mo(CO)_3$ads was exposed to P_{CO} = 1 atm at −17° for 15 min, the system was evacuated and then swept with helium for 15 min. Sweeping the product with helium at 100° for 40 min released 1.04 ± 0.08 CO/Mo.

A flow of carbon monoxide at 100° passed over $Mo(CO)_3$ads (either freshly prepared or after use as a catalyst for the disproportionation of propylene) results in the removal of about 90% of the original $Mo(CO)_3$ads as molybdenum hexacarbonyl collected in a trap at −78°. This de-