dry benzene and heated at 68 °C for 24 h. Upon cooling, the corresponding yellow acyl-rhodium complex separated (140 mg, 40% yield), but it proved difficult to purify: IR (Nujol) 2035 (C≡O), 1760, 1705 cm^{-1} (C=O); EI mass spectrum (15 eV, 180 °C), *m/z* 680, 682, 684 ($M^{+\cdot}$), 652, 654, 656 [$(M - CO)^{+\cdot}$], 624, 626, 628 [$(M - 2CO)^{+\cdot}$], 617, 619 [$(M - CO - Cl)^{+}$]; (70 eV, 130 °C, *m/z* (relative intensity) 568, 570, 572 [$(M - 4CO)^{+\cdot}$, 0.7], 540, 542, 544 [$(C_{19}H_{30}O)Rh_2Cl_2^{+\cdot}$, 0.3], 478, 480, 482 [$(C_{12}H_{10}O_3)Rh_2Cl_2^{+}$, 8.7], 450, 452, 454 [$(C_{11}H_{10}O_2)RhCl^{+}$, 14], 414, 416 [$(C_{11}H_9O_2)$-$Rh_2Cl^{+\cdot}$, 2], 386 [$(C_{10}H_9)Rh_2Cl^{+\cdot}$, 13], 241, 243 ($RhCl^{+}$, 6), 174 ($C_{11}H_{10}O_2^{+\cdot}$, 48), 146 ($C_{10}H_{10}O^{+\cdot}$, 48), 118 ($C_9H_{10}^{+\cdot}$, 85), 117 ($C_9H_9^{+}$, 100), 91 ($C_7H_7^{+}$, 33), 78 ($C_6H_6^{+\cdot}$, 46), 77 ($C_6H_5^{+}$, 80), 66 ($C_5H_6^{+\cdot}$, 52).

A solution of 140 mg of the adduct in hot benzene was treated with 150 mg of triphenylphosphine, the yellow rhodium complex was filtered off, and the filtrate was separated on 15% OV-101/Chromosorb W at 165 °C to give 21 mg (35% from the adduct) of *endo*-tricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one (**9**) (identical in all properties with those of an authentic sample[10]) and 46 mg of octahydro-1,3,5-methenocyclopenta[*cd*]pentalen-2,4-dione (**8**); mp 213-214 °C (lit.[12] 213-214 °C); IR and ^1H NMR spectra were consistent with those reported;[12] EI mass spectrum (70 eV, 25 °C), *m/z* (relative intensity) 174 ($M^{+\cdot}$, 40), 146 (20), 118 (85), 117 (100), 115 (30), 91 (35), 77 (25), 76 (25), 68 (40), 65 (30), 64 (25), 50 (30), 38 (55).

Reaction of Decahydro-1,2,4-methenocyclobut[*cd*]indene with $Rh_2(CO)_4Cl_2$. A mixture of 520 mg of **7**, 680 mg of $Rh_2(CO)_4Cl_2$ and 25 mL of dry benzene was heated in a pressure tube at 80 °C. After 72 h the dark solution was filtered through alumina and separated on 15% OV-101/Chromosorb W at 200 °C to give 286 mg (56%) of **10**[26] and 171 mg (28%) of colorless decahydro-1,3,5-metheno-1*H*-cyclopent[*cd*]inden-2-one (**11**): mp 128-130 °C; IR (CCl_4) 1766 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.488-1.569 (m, H_4, $H_{4'}$, H_6, $H_{6'}$), 1.588 (7, H_{4a}), 1.685 (m, H_7, $H_{7'}$), 1.821 (m, H_5, H_{7b}), 1.970 (m, H_8), 2.144 (m, H_{7a}), 2.314 (m, H_{2a}, H_3), 2.562 (m, H_1). Anal. Calcd for $C_{12}H_{14}O$: C, 82.8; H, 8.1. Found: C, 82.8; H, 8.0.

Conversion of 3,5-Dimethyloctahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene (6) into *endo*-3,10-Dimethyltricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene (12). A mixture of 120 mg of **6**, 60 mg of $Rh_2(CO)_4Cl_2$, and 3 mL of benzene was heated in a pressure tube at 110 °C for 48 h. Preparative GC on 15% OV-101/Chromosorb W (130 °C) afforded 80% of diene **12** as the sole product (identical with the commercial compound).

Conversion of *anti*-3-Chlorooctahydro-1,2,4-metheno-1*H*-cyclobuta[*cd*]pentalene (2, R = Cl) into *endo,anti*-3-Chlorotricyclo[5.2.1.$0^{2,6}$]deca-4,8-diene (1, R = Cl). As in the previous experiment 20 mg of **2** (R = Cl), 26 mg of $Rh_2(CO)_4Cl_2$, and 1 mL of benzene were heated at 80 °C for 5 days. GC analysis indicated the formation of **1** (R = Cl)[9] as the only product.

Kinetic Measurements. Typically a solution of 38.5 mg (0.292 mmol) of **2** (R = H) in 0.5 mL of dry degassed benzene was heated under argon in a divided airless reaction tube with the aid of an oil bath regulated at 68 ± 0.05 °C. After 20 min the solution was admixed with a solution of 56.7 mg (0.292 mequiv) of $[Rh(CO)_2Cl]_2$ and 10 μL of *n*-decane (internal standard) in 1 mL of benzene that was preheated in the second part of the reaction vessel. Samples (1-2 μL) were withdrawn periodically from the reaction mixture and immediately frozen at -78 °C. GC analysis was performed on a Varian-Aerograph Model 2800/FID instrument equipped with a 10-cm glass precolumn (to avoid any reaction from taking place at the injection port) and a 10% FFAP/Chromosorb W capillary column. The initial rates were calculated in each case from the average of at least three experiments.

Acknowledgment. The financial support of our work by the U.S.-Israel Binational Science Foundation (BSF), the Fonds der Chemischen Industrie, the exchange program between the Technical University of Berlin and the Hebrew University of Jerusalem, and the Japanese Ministry of Education are gratefully acknowledged. We also thank the Computing Center of Hokkaido University for the use of their computer.

Registry No. **1** (R = H), 1755-01-7; **1** (R = OH), 29846-26-2; **1** (R = $OCOCH_3$), 88669-65-2; **2** (R = H), 6707-86-4; **2** (R = Cl), 51965-71-0; **2** (R = OH), 15776-05-3; **2** (R = $OCOCH_3$), 55399-45-6; **3** (R = H), 56061-32-6; **3** (R = OH), 88669-66-3; **3** (R = $OCOCH_3$), 64706-13-4; **4** (R = H), 88669-69-6; **4** (R = OH), 88685-60-3; **4** (R = O), 88685-61-4; **5**, 15584-52-8; **6**, 88669-67-4; **7**, 62415-12-7; **8**, 57237-87-3; **9**, 5530-96-1; **10**, 54483-01-1; **11**, 88669-68-5; **12**, 10312-72-8; triphenylphosphine, 603-35-0; $Rh_2(CO)_4Cl_2$, 14523-22-9.

Supplementary Material Available: Table of mass spectral fragmentation data for complex **4** formed from **2** (R = H) and $Rh_2(CO)_4Cl_2$ (1 page). Ordering information is given on any current masthead page.

Sucrose Chemistry.† A Synthetically Useful Monoarenesulfonation[1a]

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The reaction of sucrose with 2,4,6-triisopropylbenzenesulfonyl chloride (tripsyl chloride) occurred preferentially at the 6'-OH group yielding crystalline 6'-*O*-tripsylsucrose (**2a**) in 39% yield without chromatography. The structure of **2a** was proven by the conversion of **2a** to the known 6'-amino-6'-deoxysucrose (**2d**) and by acid-catalyzed methanolysis which gave methyl 6-*O*-tripsyl-α- and -β-D-fructofuranoside. Also, ^1H-coupled ^{13}C NMR spectroscopy proved to be generally useful for determining substitution patterns at positions 6, 6', and 1' of sucrose. Kinetic studies of the tripsylation reaction revealed the relative reactivities of the primary OH groups at 6', 6, and 1' to be 3.5:1.0:0.16.

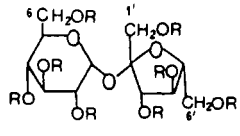
Selective reactions that distinguish between the hydroxyl groups of sucrose (**1a**) continue to be sought (see Chart I). The impetus for this search is derived from interest in the use of sucrose derivatives as noncaloric sweetening agents,[2] bacterial enzyme inhibitors,[3] surfactants,[4] food additives,[4] and resins,[4] and in other industrial applications.[4] Interest is still focused on selective derivatization of the three

† Dedicated to Professor Calvin L. Stevens on the occasion of his 60th birthday.

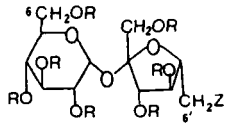
(1) (a) A preliminary account of some of this work has been presented: Taylor, K. G.; Doyle, R. J.; Singh, S.; Maynard, C. M. "Abstracts of Papers", 181st National Meeting of the American Chemical Society, Atlanta, GA, March 29-April 3, 1981; American Chemical Society: Washington, D.C., 1981; CARB 33. (b) Department of Microbiology and Immunology.

0022-3263/84/1949-0976$01.50/0

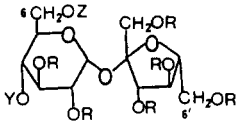
Chart I



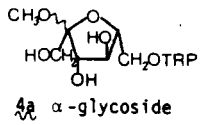
1a R = H
b R = Ac



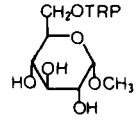
	R	Z
2a	H	OTRP
b	Ac	OTRP
c	H	N_3
d	H	NH_2



	R	Y	Z
3a	H	H	TRP
b	Ac	H	H
c	Ac	H	TRP
d	Ac	Ac	TRP



4a α-glycoside
b β-glycoside



5

primary hydroxyl groups[2,5] and selective reactions at these primary carbon atoms.[2,6] Etherification of sucrose with triphenylmethyl chloride as the limiting reagent in pyridine[5a] indicated almost equal reactivities for the OH groups at positions 6 and 6′, whereas the more sterically hindered 1′ OH group was seen to be, at most, 0.15 times as reactive. This reactivity pattern is seen with a variety of reagents which have been used to selectively make 6,6′-disubstituted sucrose derivatives. These reagents are: 2,5,6-trimethylbenzenesulfonyl chloride in pyridine, which yields thd di-*O*-arenesulfonate, and triphenylphosphine–carbon tetrachloride in pyridine,[5c] and methanesulfonyl chloride in DMF,[5d] which yield the dichloroderivative. Other workers have reported results which indicate that the hydroxyl group at position 6 is the most reactive. Thus, tris(dimethylamino)phosphine–carbon tetrachloride[5e] is reported to favor formation of 6-monosubstituted sucrose derivatives by a factor of 3 or 4 to 1. Also, the reaction of sucrose with cyanoethyl phosphate–dicyclohexylcarbodiimide in pyridine gives a 6/6′ phosphorylation ratio of 2.4.[5f]

We have reexamined the selective reaction in pyridine of 2,4,6-triisopropylbenzenesulfonyl chloride (tripsyl chloride) with sucrose (**1a**), a reagent previously reported to show low selectivity between the primary hydroxyl groups of sucrose.[7] As our preliminary report indicated,[1] tripsyl chloride does show useful selectivity in its preferential reaction with the 6′-OH group of sucrose, a result which stood in sharp contrast to the above-noted previous work. Most recently Khan has observed a similar preference for the 6′-OH group in the reaction of sucrose with *tert*-butyldiphenylsilyl chloride catalyzed by 4-(dimethylamino)pyridine in pyridine.[8] In this paper we report (1) the selective tripsylation of sucrose, (2) the chemical transformations which proved the structure of one monotripsyl sucrose derivative, which demonstrated the tripsyl group's potential in synthesis and which provided a chemical proof for the assignment of the ^{13}C resonances of carbon atoms 6, 1′, and 6′, (3) a convenient NMR spectral method for determining which of the primary sites of sucrose have been derivatized, and (4) the kinetic determination of the reactivities of primary OH groups of sucrose toward tripsyl chloride.

Tripsylation of Sucrose. Sucrose (**1a**) was dissolved in refluxing pyridine and allowed to cool. This solution, 0.2–0.3 M in **1a**, was then cooled further to −40 °C and treated by the dropwise addition of 1 equiv of tripsyl chloride in pyridine. After the addition, the reaction was allowed to warm and stand at room temperature for about 100 h. After workup, the addition of acetone:ethyl acetate:H_2O (10:10:1) produced, by slow crystallization, about 39 ± 5% yield of a white solid. This solid, which typically melted near 139–40 °C dec, proved to be the 6′-*O*-monotripsyl ester of sucrose (**2a**) contaminated with less than 5% of the 6-*O*-monotripsyl isomer (**3a**). The degree of contamination, which was monitored by high-pressure liquid chromatography (HPLC) varied from experiment to experiment. Since the amount of the isomer **3a** formed did not vary (see below) the observed variation in purity must reflect a rather delicate balance in conditions required for crystallization or cocrystallization. However, chromatography on silica gel could be used to obtain pure **2a**, mp 139–140 °C dec, in somewhat reduced yield if necessary. 4-(Dimethylamino)pyridine (DMAP) could be used to catalyze the reaction and reduce the reaction time to 24 h. The selectivity of the reaction suffered somewhat in the process, however. In addition to increased ditripsylation, we observed for the first time the appearance, in the crude reaction mixture, of a third chromatographic peak which was eluted near those of **2a** and **3a**. We have, tentatively, attributed the new peak to the 1′-*O*-tripsylsucrose isomer.[9,10] Preparative chromatography gave the following array of final products (as the corresponding polyacetates) in the DMAP-catalyzed reactions: tri-*O*-tripsylsucrose, ~5%; di-*O*-tripsylsucroses, 26–31%; mono-*O*-tripsylsucroses, 53–57% (6′:6:1′ ≈ 10:1:0.5); unreacted sucrose, 10–25%. In contrast, without DMAP, the following product distribution was obtained: tri-*O*-tripsylsucrose, <1%; di-*O*-tripsylsucroses, 19%; mono-*O*-tripsylsucroses, **2a** and **3a**, 50% (6′:6:1′ ≈ 4:1:0). Further, after collection of crystalline **2a** from the uncatalyzed reactions, slow evaporation of the filtrate yielded 4–5% of 6-*O*-tripsylsucrose (**3a**), mp 152–3 °C dec, identical with

(2) Jenner, M. R. In "Developments in Food Carbohydrate-2"; C. K. Lee, Ed., Applied Science Pub. Ltd.: London, 1980; pp 91–143.
(3) Thaniyavarn, S.; Singh, S.; Maynard, C. M.; Taylor, K. G.; Doyle, R. J. *Carbohydr. Res.* **1981**, *96*, 134.
(4) "Sucrochemistry"; Hickson, J. L., Ed.; American Chemical Society: Washington, D.C., 1977; No. 41.
(5) (a) Otake, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3199. (b) Hough, L.; Phadnis, S. P.; Tarelli, E. *Carbohydr. Res.* **1975**, *44*, c12. (c) "Methods in Carbohydrate Chemistry", Whistler, R. L., BeMiller, J. N., Eds.; Academic Press: New York, 1980, Vol VIII p. 230. (d) Khan, R.; Bhardwaj, C. L.; Mufti, K. S.; Jenner, M. R. *Carbohydr. Res.* **1980**, *78*, 185. (e) Castro, B.; Chapleur, Y.; Gross, B. *Ibid.* **1974**, *36*, 412. (f) Chassy, B. M.; Porter, E. V. *Biochem. Biophys. Res. Commun.* **1979**, *89*, 307 and private communication.
(6) The generally accepted order of "S_N2 reactivity" of the carbon atoms of sucrose is 6 ~ 6′ > 4 > 1′.[2] Recent work by Almquist and Reist has shown in one case, however, that the 6 position is the most susceptible to nucleophilic attack. Almquist, R. G.; Reist, E. J. *J. Carbohydr. Nucleosides, Nucleotides* **1979**, *3*, 261–271.
(7) Almquist, R. G.; Reist, E. J. *J. Carbohydr. Nucleosides, Nucleotides* **1974**, *1*, 461.
(8) Karl, H.; Lee, C. K.; Khan, R. *Carbohydr. Res.* **1982**, *101*, 31.
(9) It is not beyond possibility that the new, third monotripsylsucrose derivative is the 2-isomer. Tripsylation (1 equiv) of methyl α-D-glucopyranoside produced, in addition to the expected 6-*O*-tripsyl derivative, a low yield of 2,6-di-*O*-tripsyl ester as well; see Experimental Section; see also ref 10.
(10) Ballard, J. M.; Hough, L.; Phadnis, S. P.; Richardson, A. C. *Carbohydr. Res.* **1980**, *83*, 138–141.

Table I. ^{13}C NMR Chemical Shifts (δ $(CH_3)_4Si$)[a] of Sucrose (1a) and Derivatives

compd (solvent)[b]	D-gluco residue chemical shifts						D-fructo residue chemical shifts					
	C1	C2	C3	C4	C5	C6	C1′	C2′	C3′	C4′	C5′	C6′
1a (A)[c]	92.9	71.9	73.5	70.2	73.3	61.2	62.5	104.6	77.6	75.0	82.2	63.7
1a (B)[c]	92.7	72.6	73.9	71.1	73.6	61.7	63.3	105.0	78.5	75.6	83.5	63.0
2a (C)	92.1	71.9	73.5	70.4[d,e]	73.0	61.6	62.7	104.2	77.7	75.1	79.5[f]	70.6[d,e]
2a (B)	91.5	71.5[d]	72.8	70.2[d]	72.8	61.0	61.7	104.1	76.2	74.2	79.1	71.2[d]
3a (B)	91.9	71.4	72.7	69.5[d,e]	69.8[d,e]	68.5[d]	61.9	104.2	77.1	74.6	82.8	62.5
3a (C)	93.5	71.9	74.5	71.0[e]	73.0[e]	69.7	63.9	105.2	79.1	75.8	84.0	63.9
5[g] (A)	101.0	73.1	74.9	71.4[e]	71.0[e]	70.1						
4a[h] (D)							60.0	109.3	81.0	79.0	82.8	70.5
4b[i] (D)							61.2	105.7	78.5	76.9	80.3	71.3
6a[d] (D)	93.0	72.9	74.6	71.0	71.7[e]	69.9	64.1	105.7	79.5	76.3	80.9	71.9[e]
2c (A)	92.6	71.6	73.2	70.1	72.9	61.2	62.1	104.4	77.3	76.1	80.1	53.3
[j] (A)	93.0	71.9	73.4	71.4	72.1	52.0	62.6	104.8	77.7	76.5	80.5	53.8
2d (A)	93.0	71.9	73.4	70.1	73.4	61.0	62.2	104.4	77.5	76.2	82.5	48.8

[a] 1,4-Dioxane (δ 67.4), internal $(CH_3)_4Si$, or solvent signals were used as standards. [b] A: H_2O/D_2O; B: $(CD_3)_2SO$; C: CD_3OD; D: $(CD_3)_2CO$. [c] The assignments for the ring carbons are those of ref 14 and 15. [d] Assignment based on analysis of ^1H-coupled spectra.[17] [e] Assignment tentative. [f] Arenesulfonate at C6′ should deshield 6′ and shield C5′; see ref 16. [g] CH_3 resonates at δ 55.7. [h] CH_3 resonates at δ 48.7. [i] CH_3 resonates at δ 49.2. [j] 6,6′-diazido-6,6′-dideoxysucrose; ref 18.

Table II. ^{13}C NMR Chemical Shifts (δ $(CH_3)_4Si$) of Sucrose Octaacetate (1b) and Derivatives

compd (solvent)[a]	D-gluco residue chemical shifts						D-fructo residue chemical shifts					
	C1	C2	C3	C4	C5	C6	C1′	C2′	C3′	C4′	C5′	C6′
1b[b]	90.8	70.9	70.2	69.4[c]	69.1[c]	62.7	63.6	104.7	76.6	75.7	79.8	64.3
3b[b]	91.0	71.6[c]	74.0[c]	68.8[c]	72.8[c]	61.7	63.7	104.6	76.6	75.9	79.6	64.4
3c[b]	91.3	71.5	72.6	68.3[c]	71.4[c]	68.2	63.4	105.2	76.9	76.4	80.1	64.2
2b[b]	90.7	70.5	69.9	69.5[c]	69.0[c]	62.9	63.4	104.5	75.9	75.3	79.8	69.9
3d[b]	90.8	70.7	70.0	69.0[c]	68.7[c]	67.2	63.3	105.0	76.7	76.1	80.0	63.8

[a] Solvent, $(CD_3)_2CO$. [b] Assignments are based on the analysis of ^1H-coupled spectra and the analogies of refs 17 and 19. [c] Assignments tentative.

that prepared by directed synthesis (see below).

Chemical Transformations. To establish, chemically, the location of the tripsyl group in **2a** both synthetic and degradative approaches were used. First, **2a** was converted to the known, crystalline, 6′-amino-6′-deoxysucrose[11] (**2d**) by way of the glassy heptaacetate **2b** (90%) and the amorphous azide **2c** (70%). Hydrogenation of **2c** gave the aminosucrose compound **2d** in 74% yield with mp (133–135 °C) and specific rotation (+57.3°) in agreement with the published values (132–135 °C and +57.5°, respectively).[11] The overall yield of **2d** from sucrose, therefore, is on the order of 18–20%.

Acid-catalyzed methanolysis of **2a** yielded glucose and the chloroform soluble glycosides **4** in 84% yield. Crystallization from petroleum ether gave white needles (mp 89–92 °C) which proved to be an approximately 50/50 mixture of anomers. The structures of **4a** and **4b** were supported by elemental analysis and their unequivocal ^{13}C NMR spectra (see Table I). The fructofuranoside formulation is supported by the following NMR data: for **4b**, for example, two primary carbon resonances were observed at δ 61.2 (C-1) and 71.3 (C-6). In addition, no resonance for a ring carbon appeared at higher field than δ 75, a result consistent with a fructofurano structure.[12] In contrast, all the ring carbons of the isomeric methyl 6-*O*-tripsyl-α-D-glucopyranoside (**5**) resonated at higher field than δ 75 (Table I).

Analytical HPLC examination of sucrose tripsylation reactions revealed a minor monotripsyl product which was eluted ahead of **2a**. We reasoned that this was the 6-*O*-tripsyl ester (**3a**) and established that fact by alternate synthesis. The starting material for the synthesis was the known hexa-*O*-acetylsucrose derivative **3b**.[13] Treatment of **3b** with 1 equiv of tripsyl chloride gave the amorphous tripsylate **3c** in 92% yield. Acetylation of **3c** gave the heptaacetate **3d** while deacetylation with sodium methoxide in methanol gave **3a**, mp 151–153 °C dec, in 75% yield. Compound **3a** proved to be the faster eluting monotripsylate observed by HPLC in crude reaction mixtures. Its structure was confirmed by ^{13}C NMR spectroscopy as described in the next section.

^{13}C NMR Results. ^{13}C NMR chemical shifts for compounds **1–5** are collected in Tables I (nonacetylated compounds) and II (acetylated compounds). With compounds **1–3** in Table I, fairly firm chemical shift assignments could be made by making use of the firm assignments made by Jones and co-workers[14] and Bock and Lemieux[15] for sucrose (**1a**). The observation by Ball and co-workers[16] that arenesulfonation of the system C_β–C_α–OH to give C_β–C_α–CO_3SAr resulted in the deshielding of carbon α (+7 to 8 ppm) and the shielding of carbon β (-3 to 4 ppm) was also useful. Further, the analysis of ^1H-coupled ^{13}C NMR spectra assisted in identifying signal assignments because, while $^1J_{C-H}$ coupling constants for the ring carbon atoms were not diagnostically different (~140–150 ppm), the long range $^2J_{C-H}$ and $^3J_{C-H}$ couplings gave distinctive appearances to individual signals. Thus, for example,[17] C2 of α-D-glucopyranose-*5,6,6-d*$_3$ does not couple with H1, but does with H3 ($^2J_{C-H}$ = 5.5 Hz), and the half signal thereof

(11) Suami, T.; Ikedu, T.; Nishayama, S.; Adachi, R. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1953–1954.
(12) Angyal, S. J.; Bethell, G. S. *Aust. J. Chem.* **1976**, *29*, 1249–65.
(13) Khan, R. *Carbohydr. Res.* **1974**, *32*, 375–379.
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(15) Bock, K.; Lemieux, R. U. *Carbohydr. Res.* **1982**, *100*, 63–74.
(16) Ball, D. H.; Bissett, F. H.; Chalk, R. C. *Carbohydr. Res.* **1977**, *55*, 149–163.
(17) Perlin, A. S.; Cyr, N.; Ritchie, R. G. S.; Parfondry, A. *Carbohydr. Res.* **1974**, *37*, C1–C4.

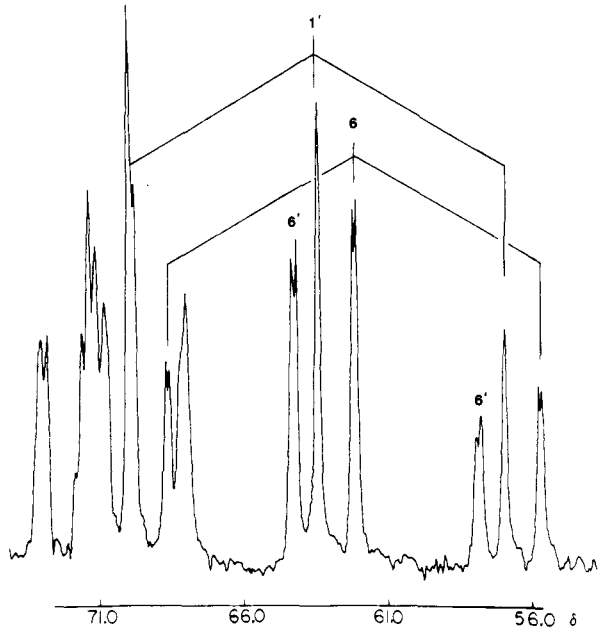

Figure 1. Partial ^1H-coupled ^{13}C NMR spectrum of sucrose (**1a**). See text for discussion.

appears as a rather sharp doublet. In contrast, C3 couples with H2 and H1 and its half signal appears as a quartet.[17] Thus, in the 1H-coupled spectra of compounds **1–3** the half signal of C2, where observable, was characteristically a doublet, while that of C3 was a multiplet. In the case of the compounds in Table II, the assignments of **1b** were made with the assistance of the work of Gagnaire and co-workers[19] who used selective ^1H decoupling to assign the ^{13}C resonances of a number of acetylated D-glucopyranose and D-glucopyranoside derivatives.

Importantly, ^1H-coupled ^{13}C NMR spectra enabled the facile identification of the patterns of substitution on the primary carbon atoms of sucrose. Figure 1 shows a ^1H-coupled spectrum of the primary carbon resonances of sucrose. The high-field two-thirds of the triplets (^1J's ~ 142–145 Hz) resulting from $^1J_{C-H}$ are discernable. The key feature of the pattern is the narrower, more intense signal of the resonance of C-1′ relative to the flanking signals of C-6′ and C-6. We assume that the broadening (and the consequent "shortening") of these two signals results from the additional $^2J_{C-H}$ coupling that they experience (from H-5′ and H-5). This pattern of relative intensities (and signal widths) remained apparent in spectra with poorer resolution and lower S/N ratios. A case in point is shown in Figure 2 which shows a partial spectrum of **2a**. A ^1H-decoupled spectrum of **2a** shows two signals in the $-CH_2OH$ spectral region. In the coupled spectrum of Figure 2 the high-field two-thirds of the triplets resulting from $^1J_{C-H}$ are clearly discernible, and from the relative intensities it can be seen that the flanking resonance accompanying that of C-1′ is its high-field companion (C-6). C-6′, thus, must carry the tripsylate group and resonate downfield (see Table I). In the coupled spectrum of **2c**, the immediate precursor of the known amino sucrose **2d**, the two $-CH_2OH$ resonances displayed the same relative intensity pattern, with the more intense C-1′ resonance again accompanied by the less intense, broader high-field companion (C-6). In this case the $-CH_2N_3$ group (C-6′) was seen as a triplet at higher field, δ ~53, with its signals having intensities similar to those of C-6. With the conversions of **2c** to **2d** and **2a** to **4** we have provided chemical proof for the ^{13}C resonance assignments of carbons 6,1′, and 6′ first given chemical support by Hough et al.,[20] further suggested by Jones et al.,[4] and ascertained spectrally by Bock and Lemieux.[15]

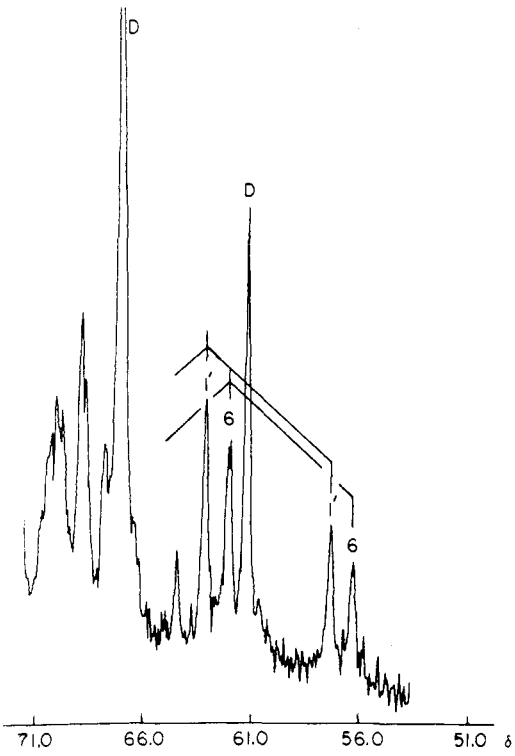

Figure 2. Partial ^1H-coupled ^{13}C NMR spectrum of **2a**. The signals labeled D are due to 1,4-dioxane internal standard. See text for discussion.

Kinetic Studies. With the obtainment of **2a** as the major product of the monotripsylation reaction we saw an opportunity to obtain "semiquantitative" measures of the reactivities of the primary hydroxyl groups of sucrose toward this arenesulfonation reagent. Toward this end we measured the early rates of conversion of sucrose (**1a**) to **2a**, and **2a** to di-*O*-tripsylsucrose using HPLC analysis to monitor the rate of appearance of **2a** and di-*O*-tripsylsucrose, respectively.

The solvent composition (35% CH_3CN in H_2O) required to chromatographically separate **2a** from **3a** was not suitable for analyzing reaction aliquots of kinetic runs. Thus, 50% CH_3CN/H_2O was used and the rates of formation of **2a** plus **3a** were monitored over the first 30 min of reaction. The resulting rate constant was partitioned according to the ratio of **2a**/**3a** ascertained in a separate analysis using 35% CH_3CN/H_2O. The ratio of **2a**/**3a** increased gradually over time, being 3.5 after 1 h and rising to 4.0 after 96 h in a reaction originally 0.19 M in **1a** and tripsyl chloride. This change may be due to the (expected) more rapid conversion of **3a** than of **2a** to 6,6′-di-*O*-tripsylsucrose. Also, the slow conversion of **3a** to 6-chloro-6-deoxysucrose might be involved.[6,20] For tripsylations 0.19 M in both **1a** and tripsylchloride in pyridine, at 24 °C, we obtained an overall rate constant after 30 min reaction of 0.029 ± 0.005 L mol^{-1} min^{-1} (average of 3 runs). If a partitioning ratio of 3.5:1 is used, the rate constant for formation of **2a** is 0.023 ± 0.005 L mol^{-1} min^{-1} and that for formation of **3a** is 0.006 ± 0.005 L mol^{-1} min^{-1}.

(18) Almquist, R. G.; Reist, E. J. *Carbohydr. Res.* **1976**, *46*, 33–41.
(19) Gagnaire, D. Y.; Taravel, F. R.; Vignon, M. R. *Carbohydr. Res.* **1976**, *51*, 157–168.
(20) Hough, L.; Phadnis, S. P.; Tarelli, E., Price, R. *Carbohydr. Res.* **1976**, *47*, 151–154.
(21) Hough, L.; Mufti, K. S. *Carbohydr. Res.* **1972**, *25*, 497–503.

As a check on the rate of tripsylation of position 6 of sucrose the monotripsylation of **2a** was briefly examined. This reaction produced, according to HPLC analysis, two ditripsylsucrose compounds in a ratio of about 6:1. Careful chromatography of a monotripsylation of sucrose yielded fractions containing mostly the major isomer from which a solid product, mp 90–95 °C, was obtained. It had the same HPLC retention volume as the more abundant ditripsyl product and ^{13}C NMR analysis (Table I) indicated that it was the 6,6′-di-*O*-tripsylsucrose isomer (**6a**). The overall rate constant for formation of **6** from **2a** (0.19 M in reactants at 24 °C in pyridine) was 0.005 ± 0.0004 L mol^{-1} min^{-1}. Using the partitioning factor of 6:1 we obtain a rate constant for the formation of **6a** of 0.0043 L mol^{-1} min^{-1}, a value consistent with that as described above. The relative reactivities toward tripsyl chloride of the OH groups at 6′:6:1′ are then roughly 3.5:1.0:0.16.

Experimental Section

General Procedures. ^{13}C NMR spectra were recorded at 22.63 and 75.43 MHz on Bruker WH90-DS and Varian XL300 spectrometers. Optical rotations were measured on a Perkin-Elmer Model A241 Polarimeter. High-pressure liquid chromatography (HPLC) was performed on Waters Associates Model M-600A and Varian Associates Model 5000 instruments fitted with variable wavelength UV detectors. Whatman Partisil PXS 10/25 ODS-2 columns were used. Other chromatographic details are noted below as required. Melting points were obtained with a Thomas-Hoover apparatus and are uncorrected. Microanalyses were performed by Midwest Microlabs, Inc., Indianapolis, IN, 46250.

6′-*O*-Tripsylsucrose (2a). Sucrose, 5.0 g (0.015 mol), was dissolved with heating in 65 mL of pyridine (concentration, 0.22 M). The solution was cooled to −40 °C, and 4.5 g (0.015 mol) of tripsyl chloride was added and dissolved by stirring the mixture under N_2 atmosphere at −40 °C. After 1 h the temperature was allowed to rise to room temperature and stirring was continued for 100 ± 10 h. The solution was cooled to 0 °C, 25 mL of H_2O was added dropwise, and the mixture was stirred at room temperature for 2 h. The solvents were distilled in vacuo and the last traces of H_2O and pyridine were removed by codistillation with 100 mL of xylene (two times in vacuo at 50 °C). The residue was mixed with 50 mL of H_2O and this mixture was extracted with ethyl acetate (2 × 200 mL). The ethyl acetate solution was dried and evaporated in vacuo. The last traces of H_2O were removed by codistillation with toluene as before. The resulting solid residue was dissolved in a minimum volume of acetone:ethyl acetate:H_2O (10:10:1 by vol) and the solution was cooled for 24 h in a refrigerator to yield a white crystalline solid. Filtration and washing with 50 mL of acetone:ether (1:1 by vol) gave 3.5 g (39%) of **2a**: mp 139–140 °C dec; $[\alpha]^{24}_D$ +51.4° (*c* 1, CH_3OH); UV λ_{max} (95% C_2H_5OH) 231 nm (ε 9800), 278 (2400), 285 (2300). Compound **2a** thus prepared displayed a single peak on HPLC analysis under conditions which separated **2a** from **3a**. Retention time: 9.7 min (flow rate, 2 mL min^{-1}; solvent, 35% CH_3CN by vol in H_2O; detector, 280 nm). Compounds **2a** and **3a** were not separated by CH_3CN–H_2O mixtures having more than 40% CH_3CN nor by any CH_3OH-based solvent mixtures.

Anal. Calcd for $C_{27}H_{44}O_{13}S$: C, 53.28; H, 7.25; S, 5.26. Found: C, 53.13; H, 7.46; S, 5.24.

The filtrate was allowed to evaporate at room temperature for 2 days. The resulting solid was separated by filtration and washed with 20 mL of ethyl acetate to give 0.4 g (4.5%) of **3a**: mp 152–153 °C dec; $[\alpha]^{24}_D$ +39.2° (*c* 1, CH_3OH). Compound **3a** thus isolated displayed a single peak on HPLC analysis under conditions which separated **2a** from **3a**. retention time: 8.5 min (flow rate, 2 mL min^{-1}; solvent, 35% CH_3CN by vol in H_2O; detector, 280 nm). Compound **3a** thus isolated was identical with that prepared by an independent route (see below).

When the above described tripsylation was repeated with 0.5 g of 4-(dimethylamino)pyridine (DMAP) added, reaction times were reduced. Thus the same work up after 1 or 2 days yielded 8 g of solid after ethyl acetate extraction and evaporation. HPLC analyses of such preparations indicated the presence of a third compound with a retention time appropriate for a monotripsyl sucrose derivative, 11.8 min (2 mL min^{-1}; 35% CH_3CN by vol in H_2O). Tentatively, its structure is assigned as 1′-O-tripsylsucrose (see text). Crystallizations of these preparations produced mixtures. Accordingly, 8 g of the product was charged onto a silica gel column (350 g) and eluted with acetone:ethyl acetate:H_2O (10:10:1 by vol). Compound **2a** began crystallizing in collection tubes. Fractions having a TLC component at R_f 0.2 (same solvent system) were combined and concentrated. The residue was crystallized from the above elution solvent system in a refrigerator to yield 3.3 g (36%) of **2a**: mp 139–140 °C dec; $[\alpha]^{24}_D$ + 5.14° (*c* 1, CH_3OH). The filtrate was concentrated to yield 1.8 g (20%) of a solid which, by HPLC analysis, consisted of **3a**, **2a**, and 1′-*O*-tripsylsucrose in the approximate ratios of 1:4:0.5. Chromatography fractions with TLC components at R_f 0.4 were combined and concentrated to yield 2.75 g (31%) of solid which, by ^1H NMR characterization, was a mixture of di-*O*-tripsylsucrose isomers plus tri-*O*-tripsylsucrose.

If the DMAP-catalyzed tripsylation reaction were followed by acetylation with excess acetic anhydride, the corresponding polyacetates were obtained. Careful chromatography of this mixture failed to produce pure components but did indicate the following approximate yields of classes of compounds (as the poly-*O*-acetates): tri-*O*-tripsylsucrose, 5%; di-*O*-tripsylsucroses, 17%; mono-*O*-tripsylsucroses, 45%; sucrose, 25%.

6′-*O*-Tripsyl-2,3,4,6,1′,3′,4′-hepta-*O*-acetylsucrose (2b). A solution of 2.0 g (0.0033 mol) of **2a** in 30 mL of pyridine and 6.0 mL of acetic anhydride was stirred at room temperature for 24 h. The reaction liquids were distilled in vacuo to dryness and the resulting residue was extracted with ether (3 × 50 mL). The ether extracts were washed (saturated $NaHCO_3$ and H_2O), dried ($MgSO_4$) and evaporated to give 2.7 g (90%) of **2b** as an amorphous solid: mp 66–71 °C; TLC (ether), one spot at R_f 0.36; $[\alpha]^{21}_D$ +46.3° (*c* 1.7, $CHCl_3$).

Anal. Calcd for $C_{41}H_{58}O_{20}S$: C, 54.54; H, 6.43; S, 3.54. Found: C, 54.42; H, 6.75; S, 3.45.

6′-Azido-6′-deoxysucrose (2c). A solution of 0.903 g (0.001 mol) of **2b** plus 0.390 g (0.006 mol) of NaN_3 in 20 mL of HMPA was stirred and heated at 120–125 °C for 24 h. The cooled reaction mixture mixture was poured into 200 mL of a stirred, ice-containing 20% NaCl solution. This mixture was extracted with ethyl acetate (3 × 100 mL) and the combined extracts were evaporated to give a white foam. The foam was slurried with 50 mL of acetone, the slurry was filtered, the filter cake was washed with acetone, and the filtrate was evaporated to dryness. The resulting residue was dissolved in ether; the ethereal solution was washed with 5% NaCl solution, washed with H_2O, dried (Na_2SO_4), and evaporated to give a glassy solid. This solid was subjected to deacetylation using stirred $NaOCH_3$ in CH_3OH (20 mL at pH 8) for 6 h. Neutralization with Amberlyst 15 resin, filtration, and evaporation of the filtrate produced a solid which was dissolved in 30 mL of H_2O. This solution was continuously extracted with $CHCl_3$ for 10 h. The aqueous layer was decolorized with charcoal, filtered through Celite, and evaporated to dryness. The residue was dried (P_2O_5) in vacuo to give 0.257 g (70%) of an amorphous solid, **2c**: TLC ($CHCl_3$: CH_3OH, 3:1 by vol) showed one spot, R_f 0.3; $[\alpha]^{21}_D$ +68° (*c* 1, H_2O). All attempts to crystallize **2e** failed and it was used directly in the next reaction.

6′-Amino-6′-deoxysucrose (2d). To a solution of 1.23 g (0.0033 mol) of **2c** in 50 mL of CH_3OH was added 0.65 g of 10% Pd on charcoal. The resulting mixture was hydrogenated at 270 kPa (40 lbs $in.^{-2}$) in a Paar hydrogenation apparatus for 24 h. The mixture was filtered through Celite, the filtrate was evaporated to dryness, and the residue was dissolved in a minimum volume of C_2H_5OH:CH_3OH:H_2O (3:3:4 by vol). Storage of the solution in a refrigerator slowly gave 0.85 g (74%) of crystalline **2d**: mp 133–135 °C dec; $[\alpha]^{19}_D$ + 57.3° (*c* 1, H_2O) [lit.[17]: mp 132–135 °C dec; $[\alpha]^{24}_D$ + 57.5° (*c* 1.8, H_2O).

6-*O*-Tripsyl-2,3,1′,3′,4′,6′-hexa-*O*-acetylsucrose (3c). A solution of 0.750 g (0.00126 mol) of **3b**[13] in 50 mL of pyridine containing 2.0 g (0.0066 mol) of tripsyl chloride was stirred at room temperature for 1 week. The reaction mixture was cooled to 0 °C, and 10 mL of water was added. The resulting mixture was stirred for 1 h at room temperature and then evaporated to dryness in vacuo. The residue was extracted with ether, and the extract was washed with water and then dried ($MgSO_4$). Concentration of the ether solution gave a syrup which was chromatographed

on silica gel. Elution with ethyl acetate:light petroleum ether (3:2 by vol) gave 1.0 g (92%) of crystalline **3c**: mp 62–65 °C; $[\alpha]^{24}_D$ + 37.9° (*c* 2.1, $CHCl_3$).

Anal. Calcd for $C_{39}H_{56}O_{19}S$: C, 54.42; H, 6.50%. Found: C, 54.90; H, 6.55.

6-*O*-Tripsyl-2,3,4,1′,3′,4′,6′-hepta-*O*-acetylsucrose (3d). A solution of 1.0 g (0.0012 mol) of **3c** in 15 mL of pyridine and 5 mL of acetic anhydride was stirred at room temperature for 20 h. The reaction mixture was evaporated to dryness and the residue was dissolved in ether. The ether solution was washed (10% $NaHCO_3$ and H_2O), dried ($MgSO_4$), and evaporated to give 1.0 g of **3d** as a glassy solid. Chromatography on silica gel (ethyl acetate:light petroleum ether, 1:2 by vol) did not seem to improve the purity of **3d**: mp 55–58 °C; $[\alpha]^{21}_D$ +52.8° (*c* 1.15, $CHCl_3$); TLC (ether), one spot, R_f 0.36. While heptaacetates **2b** and **3d** were readily separated by HPLC (solvent, ethylacetate–hexane, 1:1 by vol; flow rate, 1 mL min^{-1}), they could not be separated by TLC on silica gel in a variety of solvent systems and, consequently, were not separable on preparative scale chromatography on silica gel.

6-*O*-Tripsylsucrose (3a). A solution of 1.5 g (0.0017 mol) of **3d** in 50 mL of CH_3OH containing CH_3ONa (pH 8) was stirred at room temperature for 8 h. The solution was neutralized with Amberlyst 15 (H^+) resin and filtered, 2 mL of triethylamine was added, and the solution was evaporated to dryness. The residue was crystallized and recrystallized from CH_3OH to give 0.75 g (75%) of **3a**: mp 151–153 °C dec; $[\alpha]^{22}_D$ +39.0° (*c* 0.13, CH_3OH). Compound **3a** thus prepared was identical chromatographically and spectrally with that isolated from the tripsylation of sucrose.

Anal. Calcd for $C_{27}H_{44}O_{13}S$: C, 53.28; H, 7.25; S, 5.26. Found: C, 52.98; H, 7.19; S, 5.06.

Methyl 6-*O*-Tripsyl-α- and -β-D-fructofuranoside (4). A solution of 1.50 g (0.0025 mol) of **2a** in 60 mL of CH_3OH and 0.25 mL of trifluoroacetic acid was refluxed for 20 h. The liquids were distilled in vacuo and the residue was extracted with ethyl acetate (2 × 50 mL). The ethyl acetate solution was washed (5% $NaHCO_3$ solution, H_2O), dried ($MgSO_4$), filtered, and evaporated to give 1.12 g of solid. HPLC analysis of the solid (50% CH_3CN/H_2O, flow rate, 1 mL min^{-1}) showed 3 components: **2a** (trace) at 1.50 min, **4b** at 7.10 min, and **4a** at 8.30 min. The ratio of **4b** to **4a** was 1.25:1. The solid was charged onto a silica gel column. Elution with ethyl acetate gave 0.95 g (84%) of a mixture of **4a** and **4b**; crystallization from ether–petroleum ether (1:1) gave a **4a** and **4b** mixture as white needles, mp 89–92 °C; $[\alpha]^{24}_D$ + 10.0° (*c* 1, $CHCl_3$); ^{13}C NMR spectroscopy (Table I) indicated that the crystals were approximately a 1:1 mixture of **4a** and **4b**.

Anal. Calcd for $C_{22}H_{36}O_8S$: C, 57.39; H, 7.82; S, 6.95. Found: C, 57.12; H, 7.88; S, 6.74.

Extensive efforts to chromatographically separate **4a** and **4b** finally gave small amounts of pure **4a** (TLC, R_f 0.38; solvent, ethyl acetate) and **4b** (R_f, 0.32) which did not crystallize. ^{13}C NMR spectroscopy was used to assign the anomeric configurations. The crystalline mixture of **4a** and **4b** gave a ^{13}C NMR spectrum which was the sum of the spectra of **4a** and **4b**.

Methyl 6-*O*-Tripsyl-α-D-glucopyranoside (5). A solution of 5.8 g (0.030 mol) of methyl α-D-glucopyranoside and 9.06 g (0.030 mol) of tripsyl chloride in 150 mL of pyridine was stirred at room temperature for 60 h. Workup as with **2a** gave 10 g of crude product. HPLC (solvent, 85% CH_3OH in H_2O by vol; flow rate, 1 mL min^{-1}) indicated two tripsyl-bearing products which were separated by chromatography on silica gel: elution with $CHCl_3$:acetone (7:3 by vol) yielded 2 g of a ditripsyl product, mp 72–73 °C, $[\alpha]^{20}_D$ + 37° (*c* 1, CH_3OH), tentatively formulated as methyl 2,6-di-*O*-tripsyl-α-D-glucopyyranoside.

Anal. Calcd for $C_{37}H_{58}O_{10}S_2$: C, 61.15; H, 7.98; S, 8.81. Found: C, 61.29; H, 7.95; S, 8.89.

Elution with $CHCl_3$:acetone (2:1 by vol) yielded 6 g (43%) of crystalline **5**: mp 142–143 °C; $[\alpha]^{20}_D$ + 70.1° (*c* 1, CH_3OH).

Anal. Calcd for $C_{22}H_{36}O_8S$: C, 57.39; H, 7.82; S, 6.95. Found: C, 57.48; H, 7.84; S, 6.99.

6,6′-Di-*O*-tripsylsucrose (6a). The tripsylation of 5.0 g of sucrose was carried out as previously described. The resulting crude solid, 8.5 g, was charged on to a silica gel column and eluted with $CHCl_3$/acetone (1:1 by volume). Fractions of 20 mL were collected and the ditripsyl isomers appeared in fractions 13–120. HPLC analysis (solvent, CH_3OH; flow rate, 1 mL min^{-1}) of the crude reaction mixture showed three peaks in the "ditripsylate region" of the chromatogram eluting at 2.7, 3.0, and 3.6 min. The largest peak, the 6,6′-isomer, was the peak eluted at 3.0 min, and it was the major component (estimated 95%) in the column chromatography fractions numbered 35–111. Concentration and cooling of the combined fractions gave 2.0 g (15%) of 6,6′-di-*O*-tripsylsucrose, mp 90–95 °C.

Anal. Calcd for $C_{42}H_{66}O_{15}S_2$: C, 57.69; H, 7.55; S, 7.32. Found: C, 57.47; H, 7.75; S, 7.18.

Kinetic Studies. All glassware was flame dried under a sweep of dry N_2 before use and/or after assembly. Sucrose (pulverized) and tripsyl chloride (recrystallized) were dried over P_2O_5 in vacuo, and pyridine was distilled from CaH_2 and stored over NaOH shortly before use. All liquid transfers were performed by using syringes, and the reaction vessels were sealed with rubber septa. UV detector response factors, at 280 nm, were calculated by using solutions of **2a** and **6a** and the internal standards *N,N*-dimethyl-2,4,6-triisopropylbenzenesulfonamide, mp 122.5 °C (calcd for $C_{17}H_{29}NO_2S$, C, 65.55; H, 9.38; found, C, 65.77; H, 9.55), or *o*-dichlorobenzene. Tripsylation reactions were conducted at 24 °C under N_2 atmosphere. Aliquots were withdrawn by syringe and quenched in 50% CH_3CN/H_2O prior to HPLC analysis. The rate of appearance of **2a** or **6** was measured by integration of the appropriate chromatographic peak and the concentration was calculated with reference to the appropriate internal standard. Second order kinetics were assumed and the rate constants calculated from plots of $(X/[S]_0([S]_0 - X))$ vs. time.

Sucrose. About 1 g of sucrose was dissolved in hot pyridine. The solution was cooled to 24 °C and the internal standard and about 0.9 g of tripsyl chloride were added in enough pyridine to make the final concentrations about 0.2 M (15 mL total volume). Aliquots were removed and quenched at t = 0 and at 3 min intervals thereafter until 30 min had elapsed. The quenched 10-μL aliquots were analyzed by HPLC under the following conditions: solvent, 50% CH_3CN in H_2O; column temperature, 29 °C; flow rate, 1 mL min^{-1}. Both the sulfonamide and *o*-dichlorobenzene were used as internal standards. Aliquots of the kinetic runs as well as specially prepared and quenched samples were analyzed by HPLC using 35% acetonitrile in H_2O to determine the **2a**/**3a** ratio.

6′-*O*-Tripsylsucrose. About 0.4 g of **2a**, 0.25 g of tripsyl chloride, and 0.2 g of *o*-dichlorobenzene were stirred at 24 °C in sufficient pyridine to afford solutions at 0.10 M and 0.19 M. Aliquots of 10 μL were taken every 30 min for up to 150 min and analyzed by HPLC under the following conditions: solvent, 50% CH_3CN in H_2O; column temperature, 29 °C; flow rate from t = 0 to t = 10.0 min, 1 mL min^{-1}; flow rate from t = 10.0 min to the end (~15 min), 3 mL min^{-1}. The isomeric ditripsylates are resolved under these conditions.

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Registry No. **1a**, 57-50-1; **2a**, 88854-65-3; **2b**, 88854-67-5; **2c**, 82540-69-0; **2d**, 56720-34-4; **3a**, 88854-66-4; **3b**, 52706-47-5; **3c**, 88854-68-6; **3d**, 88854-69-7; **4a**, 88854-70-0; **4b**, 88854-71-1; **5**, 88854-72-2; **6a**, 88854-74-4; tripsyl chloride, 6553-96-4; 1′-*O*-tripsylsucrose, 88866-98-2; di-*O*-tripsylsucrose, 88854-75-5; tri-*O*-tripsylsucrose, 88854-76-6; methyl α-D-glucopyranoside, 97-30-3; 2,6-di-*O*-tripsyl-α-D-glucopyranoside, 88854-73-3.