BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3660—3667 (1972)

Inositol Derivatives. V. Selective Benzoylation of 1,2-*O*-Cyclohexylidene-*myo*-inositol and Preparation of New *O*-*p*-Tolylsulfonyl-*myo*-inositols

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(Received May 30, 1972)

The reaction of 1,2-*O*-cyclohexylidene-*myo*-inositol (**1a**) with 1.5 equiv. of benzoyl chloride below 0°C gave 3-*O*-benzoate (**2a**) predominantly in 40% yield, together with easily separable 3,6-di-*O*-benzoate (**3a**) in 2.5% yield. Selective sulfonylation of **2a** gave three new *O*-*p*-tolylsulfonyl-*myo*-inositols (the 4,6- (**8a**), 4,5- (**9a**), and 4,5,6-*p*-toluenesulfonates (**10**)). From **3a**, two *O*-*p*-tolylsulfonyl derivatives (5- (**15a**) and 4,5-*p*-toluenesulfonates (**16**)) were obtained. The relative reactivities, toward benzoylation, of the hydroxyl groups of **1a** were shown to be almost similar to those observed in tosylation. The *p*-tolylsulfonyloxy function on C-5 of **10** was found to be readily displaced preferentially by chloride ion.

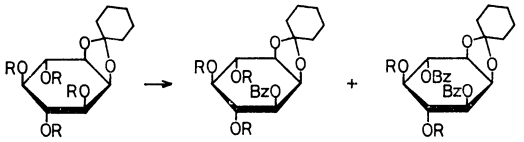
As the continuation to a program[1] to elucidate relative reactivities of hydroxyl groups of cyclitols toward esterification, a selective benzoylation of 1,2-*O*-cyclohexylidene-*myo*-inositol (**1a**)[2] was studied. We wish to report on the preparation of two benzoates by selective benzoylation of **1a**, from which four new *p*-toluenesulfonates of *myo*-inositol were obtained by

1) T. Suami, S. Ogawa, T. Tanaka, and T. Otake, This Bulletin, **44**, 835 (1971); T. Suami, S. Ogawa, and S. Oki, *ibid.*, **44**, 2820, 2824 (1971).

2) S. J. Angyal, M. E. Tate, and S. D. Gero, *J. Chem. Soc.*, **1961**, 4116.

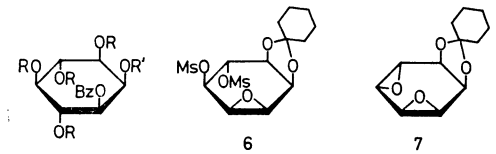
sulfonylation. Preferential replacement of the *p*-tolylsulfonyloxy function with chlorine atom in dry pyridine in the presence of pyridine hydrochloride was observed at elevated temperature.

The reaction of **1a** with 1.5 equiv. of benzoyl chloride in dry pyridine at −5—0°C for 3 days gave, in 40% yield, the 3-*O*-benzoate (**2a**) as the sole crystalline monobenzoate together with a considerable proportion of a mixture of the di- and tri-benzoates, from which the 3,6-di-*O*-benzoate (**3a**) was readily isolated in 2.5% yield by fractional crystallization. Acetylation of **2a** and **3a** in the usual way afforded the acetates (**2b**) and (**3b**), and mesylation gave the tri-*O*-mesyl derivative (**2c**) and di-*O*-mesyl derivative (**3c**), respectively.



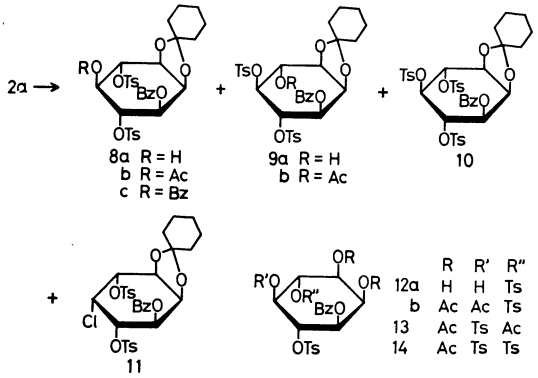
The structures of **2a** and **3a** were established by the following evidences. In analogy to the tosylation of **1a**,[1] the hydroxyl group at C–3 was also expected to be the most active toward benzoylation. Removal of the cyclohexylidene group from **2a** with boiling 80% aqueous acetic acid, followed by acetylation, gave 1-*O*-benzoyl-*myo*-inositol pentaacetate (**4**), which was proved to be identical with the compound derived from 1,4,5,6-tetra-*O*-acetyl-3-*O*-benzoyl-*myo*-inositol (**5**).[3] The proposed structure of **2a** was thus confirmed.

The reaction of **2a** with 3 equiv. of benzoyl chloride at 30°C was monitored by thin layer chromatography (tlc). After 2 days, the result was almost the same as that obtained in the reaction of **1a** with 4 equiv. of benzoyl chloride. Thus, it was clear that **3a** was formed from **2a** by further benzoylation and that an ester group was located at C–3.



When **3c** was treated with a slight excess of sodium methoxide in a mixture of chloroform and methanol, 1,2: 5,6-dianhydro-3,4-*O*-cyclohexylidene-*allo*-inositol (**7**)[4] was obtained. Since **7** can be formed from either 3,6- or 4,5-disulfonate, the structure of **3a** could be assigned to 3,6-dibenzoate. By similar treatment with sodium methoxide, **2c** afforded 2,3-anhydro-4,5-*O*-cyclohexylidene-1,6-di-*O*-methylsulfonyl-*epi*-inositol (**6**), whose proton magnetic resonance (PMR) spectrum in dimethyl sulfoxide-d_6 (DMSO-d_6) was consistent with the proposed structure, namely, the signal due to H–2 and H–3 appeared as a broad singlet at τ 6.29, and H–6 double doublet and H–1 doublet at τ 5.34 and 4.69, respectively. The up-field shift of H–6 signal might be interpreted by assuming the shielding effect above a plane of the epoxide ring in a skew conformation.[5] It is of interest to note that, in the PMR spectrum of the corresponding di-*p*-toluenesulfonate,[4] the complex multiplet (τ 6.45) due to H–2 and H–3, and H–5 triplet (τ 5.90) were only upshifted by *ca.* 0.20 ppm, as compared with those of **6**, due to the shielding effect of tosyloxy aromatic rings.

Compound **2a** may be a versatile intermediate in the synthesis of a number of inositol derivatives of biological interest. Selective sulfonylation of **2a** was carried out in order to synthesize new *O*-*p*-tolylsulfonyl-*myo*-inositols. The reaction of **2a** with 7 equiv. of *p*-toluenesulfonyl chloride in dry pyridine at room temperature (20—25°C) was monitored by tlc. After 4 days, formation of two di- and one tri-*p*-toluenesulfonates was shown by tlc. The crude mixture was then fractionated by crystallization to give 4,6-di- (**8a**) and 4,5,6-tri-*p*-toluenesulfonates (**10**) in 22 and 5% isolated yields, respectively. The oily 4,5-diester (**9a**) could be characterized by being converted into crystalline acetate (**9b**) (20% yield).



When the same reaction was carried out at 30°C for 3 days, compounds **8a**, **9b** and **10** were isolated in 30, 7, and 12% yields, respectively. Thus in view of the relative yields of the *p*-toluenesulfonates, it might be deduced that **9a** reacts with the acylating agent more rapidly than **8a** to yield **10** smoothly.

On the other hand, when the same reaction was carried out at 80—85°C, formation of an unidentified faster-moving product was observed. After 12 hr, fractionation of the crude reaction mixture by crystallization gave an unknown compound (**11**) in 9% yield, together with a mixture of **8a** and **10** (*ca.* 20%), **9b** (8%), and **10** (30%).

The acetate (**8b**) and benzoate (**8c**) were prepared in the usual way from **8a**. Removal of cyclohexylidene group from **8a** gave 1-*O*-benzoyl-4,6-di-*O*-*p*-tolylsulfonyl-*myo*-inositol (**12a**), which was converted into the triacetate (**12b**). Similarly, 1,2,6-tri-*O*-acetyl-3-

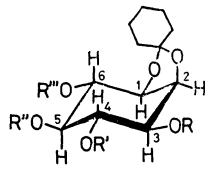
3) T. Suami, F. W. Lichtenthaler, and S. Ogawa, This Bulletin, **39**, 170 (1966).

4) T. Suami, S. Ogawa, S. Oki, and K. Ohashi, *ibid.*, **45**, 2597 (1972).

5) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press (1969), p. 99.

TABLE 1. PMR DATA[a]

Compound	R	R'	R''	R'''	H-1 ($J_{1,2}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,4}$)	H-4 ($J_{4,5}$)	H-5 ($J_{5,6}$)	H-6 ($J_{1,6}$)	OTs	OAc
1b[b]	Ac	Ac	Ac	Ac	5.74 t (5.5)	5.43 dd (3.8)	4.77 dd (9.9)	4.43 dd (8.3)	4.96 t (8.9)	4.67 dd (6.6)		7.88 7.92 7.98 7.99
1c	Bz	Bz	Bz	Bz	5.38 t (5.5)	5.08 dd (3.5)	4.34 dd (10.5)	3.71 dd (7.5)	—	— (6.5)		
2b	Bz	Ac	Ac	Ac	5.64 t (5.5)	5.26 dd (3.5)	4.53 dd (9.5)	4.26 dd (8.0)	4.84 t (8.0)	4.54 dd (6.5)		7.89 7.95 8.03
3b	Bz	Ac	Ac	Bz	5.50 t (6.0)	5.20 dd (3.5)	4.43 dd (9.5)	4.13 dd (7.5)	4.64 t (8.5)	4.38 dd (6.0)		8.02 8.07
8a	Bz	Ts	H	Ts	5.71 t (5.5)	5.40 dd (3.5)	4.55 dd (9.0)	4.84 dd (9.0)	6.12[c] t (8.0)	5.10 dd (5.5)	7.52 7.79	
8b	Bz	Ts	Ac	Ts	5.73 t (6.0)	5.39 dd (3.0)	—	—	—	— (6.0)	7.55 7.75	8.04
8c	Bz	Ts	Bz	Ts	—	—	4.10[d] d (8.0)	4.63 t (9.0)	4.17 t (10.0)	4.91 dd (6.5)	7.69 7.90	
9b	Bz	Ts	Ts	Ac	5.66 t (6.0)	5.40 dd (3.5)	4.36 dd (8.0)	4.69 dd (6.0)	5.05 dd (8.0)	4.55 dd (6.0)	7.54 7.73	7.96
10	Bz	Ts	Ts	Ts	—	—	—	—	—	—	7.55[e] 7.71	
15b	Bz	Ac	Ts	Bz	5.59 dd (5.5)	5.27 dd (3.0)	4.49 dd (10.0)	4.05 dd (9.0)	5.00 dd (9.0)	4.30 dd (7.0)	7.79	8.03
16	Bz	Ts	Ts	Bz	5.59 t (6.0)	5.31 dd (3.5)	4.37 dd (9.0)	4.57 dd (9.0)	5.02 dd (9.0)	4.30 dd (6.0)	7.69 7.73	
18	Ts	Ts	Ts	Ts	—	—	—	—	—	—	7.55[f]	
21[g]	Ts	Bz	Bz	Ts	5.63 t (5.5)	5.35 dd (3.5)	4.93 dd (9.0)	4.07 t (9.0)	4.54 t (9.0)	4.85 dd (6.0)	7.75[e]	
22	Ts	Bz	Ts	Bz	5.61 t (5.5)	5.36 dd (3.5)	4.89 dd (10.0)	4.04 dd (9.0)	4.99 t (9.0)	4.31 dd (6.0)	7.75 7.94	
23	Ts	Ts	Bz	Bz	5.58 t (6.0)	5.31 dd (3.0)	—	—	—	— (6.0)	7.54 7.81	
24	Ts	Bz	Bz	Bz	5.48 t (5.0)	5.25 dd (3.5)	4.76 dd (10.0)	3.90 t (9.0)	4.40 t (9.0)	4.18 dd (6.0)	7.78	



a) Measured at 60 MHz in $CDCl_3$, unless otherwise stated. Chemical shifts are given in τ-values. Abbreviations: d (doublet); t (triplet); dd (double doublet). First order coupling constant (Hz) are expressed. For convenience, all the compounds listed are named as derivatives of 1,2-*O*-cyclohexylidene-*myo*-inositol. b) Measured at 100 MHz. c) The signal appeared on deuteration. d) Broad doublet. e) Singlet for two methyl protons. f) Broad singlet for four methyl protons. g) Preparation of **21**, **22**, **23**, and **24** is given in Experimental.

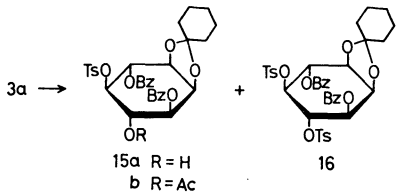
O-benzoyl-4,5-di- (**13**) and 1,2-di-*O*-acetyl-3-*O*-benzoyl-4,5,6-tri-*O*-*p*-tolylsulfonyl-*myo*-inositol (**14**) were prepared from **9b** and **10**, respectively.

Determination of the positions of the *p*-tolylsulfonyloxy groups was accomplished by means of PMR spectroscopy. In the PMR spectrum of **8a** in $CDCl_3$ (Table 1), two double doublets due to H-4 and H-6 appeared at τ 4.84 and 5.10, respectively, while H-5 triplet was observed at τ 6.12 upon addition of deuterium oxide, indicating the location of two sulfonyloxy groups at C-4 and C-6. The PMR spectrum of **9b** (Table 1) revealed the double doublet at τ 4.55, which could be assigned to H-6 signal, showing that the acetoxy group was attached at C-6.

Treatment of **9b** with excess methanolic sodium methoxide afforded **7**, excluding the 5,6-disulfonate structure of **9b**. Both the proposed structures of **8a** and **9b** were thus assigned unequivocally.

Selective sulfonylation of **3a** was conducted. The reaction of **3a** with 3 equiv. of *p*-toluenesulfonyl chloride at room temperature was monitored by tlc. After 3 days, **3a** disappeared and two mono- and one di-

p-toluenesulfonates were formed. Fractionation of the crude mixture by crystallization gave the 5-*O*- (**15a**) and 4,5-di-*O*-*p*-tolylsulfonyl derivatives (**16**) in 12 and 20% isolated yields, respectively. The faster-moving disulfonate, presumably 4-*O*-*p*-toluenesulfonate, could not be obtained in a crystalline form. However, judging from tlc, two monosulfonates seem to have been formed nearly in the same proportion.



In the PMR spectrum of the acetate (**15b**) derived from **15a**, the triplet due to H–5 appeared at higher-field (τ 5.00) as compared with H–4 double doublet (τ 4.05), indicating that the sulfonyloxy group was located at C–5.

Structural elucidation of **11** was carried out in the following way. Removal of cyclohexylidene group from **11** gave the dihydroxyl derivative (**17a**), which was transformed into the diacetate (**17b**). It was shown by elemental analyses of **11**, **17a** and **17b** that one of the tosyloxy functions of **10** was replaced by a chlorine atom. In the PMR spectrum of **11** (Fig. 1), two double doublets appeared at τ 4.73 and 4.23, having J=3.0 and 10.0 Hz, and J=4.0 and 10.0 Hz, respectively. From the coupling constants and their shapes they were clearly coupled to each other. Therefore, the former should be ascribed to the signal of the proton attached to the carbon atom bearing the tosyloxy group and the latter to that of 3-proton since it must be at the lowest field. Thus H–2, H–3, H–4, and H–5 were shown to be in equatorial, axial, axial, and equatorial arrangement, respectively. Consequently, the presence of the chlorine atom at C–5, its configuration being inverted, might only account for the above spectral data. The structure of **11** was tentatively assigned to 3-*O*-benzoyl-5-chloro-1,2-*O*-cyclohexylidene-5-deoxy-4,6-di-*O*-*p*-tolylsulfonyl-*neo*-inositol.

Mechanistically, a direct S_N2 attack of chloride ion

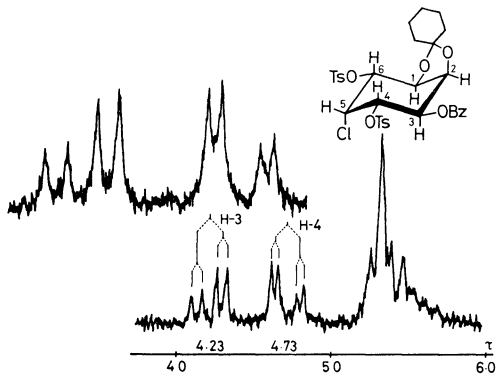


Fig. 1. Partial PMR spectrum of 3-*O*-benzoyl-5-chloro-1,2-*O*-cyclohexylidene-5-deoxy-4,6-di-*O*-*p*-tolylsulfonyl-*neo*-inositol (**11**) in $CDCl_3$ at 60 MHz. An amplified (magnification, 2) spectrum is shown above.

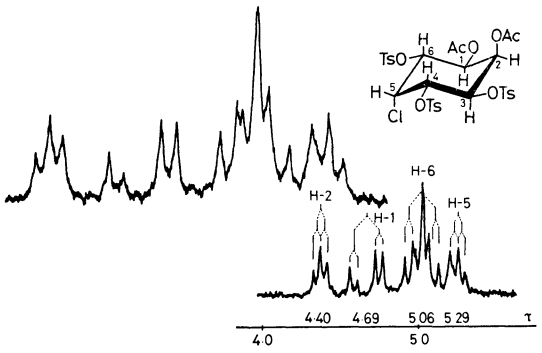
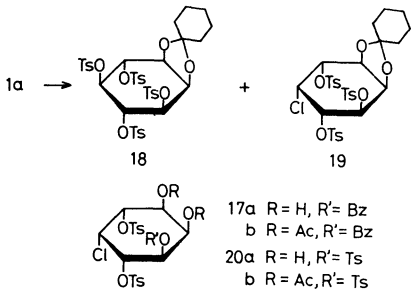


Fig. 2. Partial PMR spectrum of 1,2-di-*O*-acetyl-5-chloro-5-deoxy-3,4,6-tri-*O*-*p*-tolylsulfonyl-*neo*-inositol (**20b**) in $CDCl_3$ at 60 MHz. An amplified (magnification, 2) spectrum is shown above.

generated from pyridine hydrochloride formed might be postulated to occur at C–5 of **10**. This was supported by the following results: treatment of **10** with excess pyridine hydrochloride in dry pyridine at 90—95°C gave **11**, although in a poor yield (3.5%), but **11** could not be formed by a similar treatment of **8a**. As an analogous example, Hess and Stenzel[6] reported a facile replacement of C–6 and C–4 tosyloxy functions of methyl α-D-glucoside by treatment in dry pyridine with 6 equiv. of *p*-toluenesulfonyl chloride at 85°C.



In order to examine the proposed reaction mechanism, **1a** was subjected to similar reaction conditions yielding **11**. The expected chlorodeoxy compound (**19**) was obtained in 10% yield, together with the tetra-*O*-*p*-toluenesulfonate (**18**) (isolated yield 30%). Removal of the cyclohexylidene group from **19** gave the dihydroxyl derivative (**20a**), which was converted into diacetate (**20b**). Assuming that the displacement reaction occurred at C–5 of **18**, **19** might be formulated as 5-chloro-1,2-*O*-cyclohexylidene-5-deoxy-3,4,6-tri-*O*-*p*-tolylsulfonyl-*neo*-inositol. In the PMR spectrum of **20b** (Fig. 2), two narrow triplets appeared at τ 5.28 and 4.39, having J=2.5 and J=3.0 Hz, respectively, which were attributed to the signals of two equatorial protons (H–5 and H–2). The H–1 and H–6 signals appeared as double doublets at τ 4.69 and 5.05, having J=2.5 and 10.0, and J=3.0 and 10.0 Hz, respectively, indicating that the chlorine atom was situated axially orientated at C–5. The proposed structure was thus confirmed.

Consequently, it was demonstrated that C–5 *p*-tolylsulfonyloxy function of *p*-toluenesulfonic esters

6) K. Hess and H. Stenzel, *Ber.*, **68**, 981 (1935).

of 1,2-*O*-cyclohexylidene-*myo*-inositol was most readily replaced by chloride ion among four functions. The result is of interest in contrast to its lower reactivity toward esterification.

PMR spectra——The PMR spectra of the benzoates and sulfonates together with those of some related compounds are given in Table 1. The signals due to H–1 and H–2 could be readily assigned because they occurred up-field and were sufficiently separated from those of the protons on the remaining carbon atoms. Comparing the chemical shifts of the ring protons for **1c** with those for **1b**, the deshielding effect was observed in **1c** due to the benzoyl carbonyl group at C–3; namely, the signals for H–4, H–5, and H–6 were shifted down-field by 0.17, 0.12, and 0.13 ppm, respectively. In **3b**, H–4 and H–5 signals showed considerable down-field shifts (0.30 and 0.32 ppm) due to two ester groups at C–3 and C–6.

Interesting shielding effects on methyl signals of *p*-tolylsulfonyloxy groups were observed. The methyl protons of all the *p*-toluenesulfonates of *myo*-inositol derivatives so far reported[1] resonate in the range τ 7.54—7.59. For instance, the methyl signals of four *p*-tolylsulfonyl groups of **18** appeared at τ 7.55 as a slightly broadened singlet, whereas the introduction of benzoyl groups at vicinal positions to the *p*-tolylsulfonyloxy groups was found to cause intense up-field shifts for the methyl signals of the latter. That is, when the equatorial *p*-tolylsulfonyl group is flanked by an equatorial benzoyloxy group, the methyl signal upshifts by 0.14—0.24 ppm, and, when flanked by two, by 0.35—0.39 ppm.

It is well established that protons situated in the space above or below a benzene ring are subjected to shielding effects. The effects observed show that the benzoyloxy group adopts a conformation in which the aromatic ring is in a position at right angles to the plane of the ring of the ester group restricted of free rotation. The above effect may be applied adequately for the structural assignment of **8a** and **9b**. Thus, one of the signals of the tosyloxy methyl groups was shifted up-field by 0.20 and 0.19 ppm, respectively, showing that they were situated adjacent to the benzoyloxy group at C–3.

Experimental

Melting points were determined on a Mitamura Riken micro hot stage and are uncorrected. PMR spectra were measured on a Varian Associates A-60D (60 MHz) spectrometer at a concentration of *ca.* 10% deuteriochloroform or dimethyl sulfoxide-d_6 with tetramethylsilane as an internal standard. Chemical shifts are expressed in τ-values and signals are denoted by s (singlet), t (triplet), dd (double doublet), and m (complex multiplet). Values given for coupling constants are of first-order. Tlc was performed with silica gel (Wakogel B–10, Wako pure chemical industries Ltd.) using toluene–methyl ethyl ketone (4 : 1 or 3 : 1 volume) as the the solvent system. The compounds were detected by exposing the plate to iodine vapor or by heating after spraying 50% sulfuric acid. All solutions were concentrated by a rotary evaporator at 40—50°C under reduced pressure. All the compounds described in this paper are racemic.

3,4,5,6-Tetra-O-*benzoyl-1,2*-O-*cyclohexylidene*-myo-*inositol* (**1c**). To a solution of 1,2-*O*-cyclohexylidene-*myo*-inositol (**1a**)[2] (1.00 g) in dry pyridine (15 m*l*) was added 6 equiv. of benzoyl chloride (2.04 m*l*) under ice cooling and the mixture was kept in a refrigerator for 3 days. The solution was then poured into ice and water, and the precipitates were collected; yield 2.34 g, mp 227—241°C. By tlc, the crude crystals were shown to be contaminated with several minor components. Recrystallization from chloroform–ethanol gave colorless crystals (0.64 g, 25%) of **1c**, mp 241—243°C.

Found: C, 70.51; H, 5.05%. Calcd for $C_{40}H_{36}O_{10}$: C, 70.99; H, 5.36%.

3-O-*Benzoyl-1,2*-O-*cyclohexylidene*-myo-*inositol* (**2a**) *and 3,6-di*-O-*benzoyl-1,2*-O-*cyclohexylidene*-myo-*inositol* (**3a**). a) To a solution of **1a** (13.0 g) in dry pyridine (200 m*l*) was added, under cooling (−5—0°C), 1.5 equiv. of benzoyl chloride (8.7 m*l*) dropwise for 10 min. After being kept in a refrigerator overnight, the mixture was poured into ice and water (1 *l*). The resulting white precipitates were collected and washed thoroughly with water. The crude product (2.1 g) was recrystallized twice from methyl ethyl ketone to give colorless needles (0.58 g, 2.5%) of **3a**, mp 234—237°C. Tlc of the mother liquor indicated at least five spots: **3a**, three dibenzoates, and one tribenzoate.

Found: C, 66.85; H, 6.02%. Calcd for $C_{26}H_{28}O_8$: C, 66.65; H, 6.02%.

Evaporation of the water layer gave white crystals (5.60 g), which were recrystallized from methanol to give colorless needles (4.66 g, 39.5%) of **2a**, mp 203—205°C. From the mother liquor, an additional crop of **2a** (0.82 g) was obtained, which contained a small amount of **3a**, mp 199—205°C. Recrystallization from methanol afforded an analytical sample, mp 203.5—205°C.

Found: C, 62.87; H, 6.72%. Calcd for $C_{19}H_{24}O_7$: C, 62.62; H, 6.64%.

b) Compound **1a** (1.30 g) was treated with 1.0 equiv. of benzoyl chloride (0.58 m*l*) in dry pyridine (20 m*l*) overnight in a refrigerator, and an additional portion of benzoyl chloride (0.58 m*l*) was then added to the mixture. After being kept in a refrigerator overnight, the reaction mixture was processed as described above to give **3a** (102 mg, 4.4%), mp 234—237°C, and **2a** (569 mg, 31%), mp 200—203°C.

4,5,6-Tri-O-*acetyl-3*-O-*benzoyl-1,2*-O-*cyclohexylidene*-myo-*inositol* (**2b**). Compound **2a** (305 mg) was acetylated with acetic anhydride (4 m*l*) and pyridine (4 m*l*) overnight at room temperature. The reaction mixture was then poured into water and the crude crystals (402 mg, mp 175—177°C) were collected by suction, and then recrystallized from ethanol to afford colorless needles (344 mg, 85%) of **2b**, mp 176—178°C.

Found: C, 61.79; H, 6.27%. Calcd for $C_{25}H_{30}O_{10}$: C, 61.21; H, 6.17%.

3-O-*Benzoyl-1,2*-O-*cyclohexylidene-4,5,6-tri*-O-*methylsulfonyl*-myo-*inositol* (**2c**). To a solution of **2a** (202 mg) in dry pyridine (5 m*l*) was added methanesulfonyl chloride (0.21 m*l*, 5 equiv.) at 0°C. After being kept in a refrigerator for 2 days, the reaction mixture was poured into ice and water, and the resulting crystals (307 mg) were recrystallized from ethanol to give thin needles (239 mg, 72%) of **2c**, mp 208—210°C. An analytical sample was obtained by recrystallization from chloroform–ethanol, mp 208.5—211°C.

Found: C, 44.39; H, 5.05; S, 16.23%. Calcd for $C_{22}H_{30}O_{13}S_3$: C, 44.15; H, 5.05; S, 16.07%.

4,5-Di-O-*acetyl-3,6-di*-O-*benzoyl-1,2*-O-*cyclohexylidene*-myo-*inositol* (**3b**). Compound **3a** (195 mg) was acetylated in the same way as for **2b** to give a crude product (221 mg, mp 189—191°C), which was recrystallized from chloroform–ethanol to afford colorless rods (190 mg, 83%) of **3b**, mp 189—

192°C. Recrystallization from the same solvent gave an analytical sample, mp 192—193°C.

Found: C, 65.35; H, 6.16%. Calcd for $C_{30}H_{32}O_{10}$: C, 65.21; H, 5.84%.

*3,6-Di-*O*-benzoyl-1,2-*O*-cyclohexylidene-4,5-methylsulfonyl-*myo*-inositol (**3c**).* Compound **3a** (199 mg) was treated with methanesulfonyl chloride (0.17 m*l*, 5 equiv.) in dry pyridine (5 m*l*) in a similar way as for **2c** to give crude mesylate, which was recrystallized from chloroform–ethanol to give pure needles (181 mg, 68%) of **3c**, mp 244.5—245°C.

Found: C, 54.08; H, 5.45; S, 10.23%. Calcd for $C_{28}H_{32}O_{12}S_2$: C, 53.82; H, 5.17; S, 10.27%.

*1-*O*-Benzoyl-*myo*-inositol pentaacetate (**4**).* a) Compound **2a** (205 mg) was treated with boiling 80% aqueous acetic acid (10 m*l*) for 2 hr. The mixture was then evaporated to dryness, and the crystalline residue was acetylated with acetic anhydride and pyridine in the usual way to give a crude product (238 mg, mp 171—175°C), which was recrystallized from ethanol to afford colorless prisms (176 mg, 63%) of **4**, mp 176—180°C. An analytical sample was obtained by recrystallization from ethanol, mp 178—179°C.

Found: C, 56.27; H, 5.46%. Calcd for $C_{23}H_{26}O_{12}$: C, 55.87; H, 5.30%.

b) 1,4,5,6-Tetra-*O*-acetyl-3-*O*-benzoyl-*myo*-inositol (**5**)[3] (1.0 g) was acetylated, in the same way as for **2b**, to give crude crystals (1.02 g, mp 170—173°C), which were recrystallized from ethanol to afford pure crystals (886 mg, 81%) of **4**, mp 176—178.5°C. It was identical with the compound obtained in (a).

*2,3-Anhydro-4,5-*O*-cyclohexylidene-1,6-di-*O*-methylsulfonyl-epi-inositol (**6**).* To a solution of **2c** (82 mg) in a mixture of methanol (2 m*l*) and 2-methoxyethanol (2 m*l*) was added methanolic sodium methoxide (0.28 m*l*, equiv.) at room temperature. After 30 min, the mixture was evaporated to dryness and the residue was extracted with hot ethyl acetate. Evaporation of the extracts gave a crystalline residue which was triturated with petroleum ether and collected by suction: yield 34 mg (78%), mp 205—207°C. Recrystallization from 2-methoxyethanol afforded an analytical sample of **6**, mp 205.5—207°C.

Found: C, 42.66; H, 5.76; S, 16.43%. Calcd for $C_{14}H_{22}O_9S_2$: C, 42.20; H, 5.57; S, 16.10%.

*1,2 : 5,6-Dianhydro-3,4-*O*-cyclohexylidene-*allo*-inositol (**7**).* a) To a solution of **3c** (285 mg) in chloroform (7 m*l*) was added 1 equiv. of methanolic sodium methoxide (0.465 m*l*) and the mixture was kept in a refrigerator for 2 days. Tlc indicated one major spot together with two minor ones. The solution was then evaporated to dryness and the residue was extracted several times with hot ethyl acetate. The extracts were evaporated to give a crystalline residue, which was recrystallized from chloroform–ethanol to give colorless plates (39 mg, 38%) of **7**, mp 141—142°C. It was shown to be identical with an authentic sample.[4]

b) Compound **9b** (158 mg) was treated with 5 equiv. of methanolic sodium methoxide in a similar way to that described above to give crystals (40 mg, 87%) of **7**, mp 138—142°C.

p-*Toluenesulfonylation of **2a**. Preparation of 3-*O*-benzoyl-1,2-*O*-cyclohexylidene-4,6-di-*O*-p-tolylsulfonyl-*myo*-inositol (**8a**), 3-*O*-benzoyl-1,2-*O*-cyclohexylidene-4,5,6-tri-*O*-p-tolylsulfonyl-*myo*-inositol (**10**), and 6-*O*-acetyl-3-*O*-benzoyl-1,2-*O*-cyclohexylidene-4,5-di-*O*-p-tolylsulfonyl-*myo*-inositol (**9b**).* a) To a solution of **2a** (3.00 g) in dry pyridine (45 m*l*) was added 7 equiv. of *p*-toluenesulfonyl chloride (11.0 g) and the mixture was kept at room temperature for 4 days (20—25°C). The mixture was then poured into water (200 m*l*) and the resulting oily product was collected by decantation. It was dissolved in chloroform (100 m*l*) and washed successively with 10% aqueous sodium carbonate, N hydrochloric acid and water. After drying over anhydrous sodium sulfate, the solution was evaporated to give an oily product, which was crystallized from chloroform–ethanol to afford crystals (2.6 g). Tlc showed two major spots (**8a** and **10**). Fractional crystallization from the same solvent gave practically pure rods (1.66 g, 30%) of **8a**, mp 184—187°C, and needles (0.51 g, 7.6%) of **10**, mp 163—167°C. Analytical pure samples were obtained by recrystallization twice from the same solvent: **8a** (1.20 g, 21.6%), mp 186—188°C; **10** (0.30 g, 4.5%), mp 169—172°C.

8a: Found: C, 59.01; H, 5.32; S, 9.30%. Calcd for $C_{33}H_{36}O_{11}S_2$: C, 58.91; H, 5.39; S, 9.53%.

10: Found: C, 57.97; H, 5.17; S, 11.23%. Calcd for $C_{40}H_{42}O_{13}S_3$: C, 58.09; H, 5.12; S, 11.63%.

The mother liquor of the crude mixture was evaporated and dried by co-distillation with toluene to give a glassy product (2.11 g). A 970 mg-portion of the product was acetylated with acetic anhydride and pyridine in the usual way to give crude crystals, which were recrystallized from ethanol–toluene, affording needles (0.54 g, 19.8%) of **9b**, mp 181—184°C. Recrystallization from chloroform–ethanol gave an analytical sample, mp 182—184.5°C.

Found: C, 58.67; H, 5.33; S, 8.58%. Calcd for $C_{35}H_{41}O_{12}S_2$: C, 58.55; H, 5.76; S, 8.93%.

A 958 mg-portion of the glassy product was treated with boiling 80% aqueous acetic acid for 2 hr and the reaction mixture was evaporated to dryness, and the residue was crystallized from ethanol to give crystals (413 mg), whose tlc indicated the presence of two components. Recrystallization from ethanol–methyl ethyl ketone gave chromatographically pure crystals (55.9 mg), mp 227—228.5°C. An attempt to elucidate its structure failed. The mother liquor was evaporated to dryness and the residue was acetylated in the usual way to afford crude crystals which were recrystallized from chloroform–ethanol to give crystals (257 mg, 12%) of **13**, mp 202—205°C. This compound was identified with the compound derived from **9b**.

b) Compound **2a** (2.98 g) was treated with 7 equiv. of *p*-toluenesulfonyl chloride (11.0 g) at room temperature for 5 days. The reaction mixture was treated in a similar way to that described in (a) to give crude crystalline mixture (3.5 g) of **8a** and **10**. Fractional crystallization from chloroform–ethanol gave **8a** (0.58 g, 12.5%) and **10** (1.17 g, 17.3%) purely. The mother liquor of the crude crystals was evaporated, and, similarly, acetylated to give **9b** (1.15 g, 23%).

c) Compound **2a** (10.0 g) was treated with 7 equiv. of *p*-toluenesulfonyl chloride (36.7 g) at 30°C for 3 days. The reaction mixture was processed as described above to give crude crystalline mixture (14.9 g), from which **8a** (5.53 g, 29.8%) and **10** (2.67 g, 11.7%) were obtained by fractional crystallization. Compound **9b** (1.38 g, 7.0%) was obtained by acetylation from mother liquor.

p-*Toluenesulfonylation of **2a** at Elevated Temperature. Preparation of 3-*O*-benzoyl-5-chloro-1,2-*O*-cyclohexylidene-5-deoxy-4,6-di-*O*-p-tolylsulfonyl-neo-inositol (**11**).* a) Compound **2a** (2.95 g) was treated with 7 equiv. of *p*-toluenesulfonyl chloride at room temperature for 4 days and the reaction mixture was kept at 80—85°C for 12 hr. The mixture was poured into water and the resulting crystals (6.46 g) were collected by suction. Tlc indicated the presence of a faster-moving component together with **8a** and **10**. The mixture was fractionated by recrystallization from chloroform–ethanol to give pure crystals (1.98 g, 29.8%) of **10**, and cubic crystals (0.46 g, 9.4%) of **11**, mp 180—181°C. PMR ($CDCl_3$): τ 7.53,

7.67 (3, s, OTs C-CH_3).

Found: C, 57.56; H, 5.00%. Calcd for $C_{33}H_{35}O_{10}S_2Cl$: C, 57.34; H, 5.10%.

A crystalline mixture of **8a** and **10** (1.5 g), and **8a** (0.38 g, 8%) were isolated from the mother liquor.

b) Compound **2a** (3.03 g) was treated with 7 equiv. of *p*-toluenesulfonyl chloride at room temperature as described in (a) and the mixture was heated for 45 hr at 90—95°C. Fractional crystallization of the crude product afforded **10** (1.83 g, 31.7%), and **11** (1.03 g, 15.2%) purely.

5-O-Acetyl-3-O-benzoyl-1,2-O-cyclohexylidene-4,6-di-O-p-tolylsulfonyl-myo-*inositol* (***8b***). Compound **8a** (102 mg) was acetylated as in the preparation of **2b** to give an oily product, which was crystallized from chloroform-ethanol to afford crystals (69.4 mg, 65.2%) of **8b**, mp 124—126°C.

Found: C, 58.36; H, 5.42; S, 8.58%. Calcd for $C_{35}H_{38}O_{12}S_2$: C, 58.55; H, 5.76; S, 8.93%.

3,5-Di-O-benzoyl-1,2-O-cyclohexylidene-4,6-di-O-p-tolylsulfonyl-myo-*inositol* (***8c***). To a solution of **8a** (605 mg) in dry pyridine (11 m*l*) was added 6 equiv. of benzoyl chloride (0.63 m*l*) and the mixture was kept for 5 days at 80°C. The mixture was then poured into water and the resulting crystals (672 mg) were recrystallized from chloroform-ethanol to give colorless needles (583 mg, 84%) of **8c**, mp 195.5—198.5°C. Recrystallization from the same solvent afforded an analytical sample, mp 197—199°C.

Found: C, 61.45; H, 4.88; S, 8.57%. Calcd for $C_{40}H_{40}O_{12}S_2$: C, 61.83; H, 5.19; S, 8.26%.

1-O-Benzoyl-4,6-di-O-tolylsulfonyl-myo-*inositol* (***12a***). A mixture of **8a** (1.00 g) and 80% aqueous acetic acid (50 m*l*) was refluxed for 80 min. After being kept standing at room temperature overnight, the resulting precipitates were collected by suction: yield 0.625 g (71.0%), mp 221.5—223°C. An analytical sample was obtained by recrystallization from 2-methoxyethanol, mp 225—228°C.

Found: C, 54.53; H, 4.70; S, 10.53%. Calcd for $C_{27}H_{28}O_{11}S_2$: C, 54.72; H, 4.76; S, 10.53%.

1,2,5-Tri-O-acetyl-3-O-benzoyl-4,6-di-O-p-tolylsulfonyl-myo-*inositol* (***12b***). A mixture of **8a** (1.00 g) and 80% aqueous acetic acid (50 m*l*) was refluxed for 80 min, and then evaporated to dryness. The residue was acetylated with acetic anhydride (5 m*l*) and pyridine (5 m*l*) at 85°C for 40 min to give an oily product, which was crystallized from methanol, affording colorless plates (0.86 g, 86%) of **12b**, mp 197.5—198.5°C. An analytical sample was obtained by recrystallization from chloroform-ethanol, mp 189.5—200°C. PMR ($CDCl_3$): τ 7.55, 7.74 (3, s, OTs C-CH_3), 7.74, 8.06, 8.10 (3, s, OAc).

Found: C, 55.15; H, 4.71; S, 8.72%. Calcd for $C_{33}H_{34}O_{14}S_2$: C, 55.14; H, 4.74; S, 8.92%.

1,2,6-Tri-O-acetyl-3-O-*benzoyl-4,5-di-O-p-tolylsulfonyl*-myo-*inositol* (***13***). A mixture of **9b** (145 mg) and 80% aqueous acetic acid (10 m*l*) was refluxed for 3.5 hr and then evaporated to dryness. Tlc showed that **9b** disappeared and at least two major components were contained in the crude mixture. The residue was acetylated in the usual way to give an oily product which was crystallized from ethanol, affording colorless needles (22.3 mg, 15%) of **13**, mp 202.5—205°C. Recrystallization from chloroform-ethanol gave an analytical sample, mp 206—209°C. PMR ($CDCl_3$): τ 7.56, 7.83 (3, s, OTs C-CH_3), 7.85, 8.01, 8.02 (3, s, OAc).

Found: C, 55.13; H, 4.46; S, 8.65%. Calcd for $C_{33}H_{34}O_{14}S_2$: C, 55.14; H, 4.74; S, 8.92%.

1,2-Di-O-acetyl-3-O-benzoyl-4,5,6-tri-O-p-tolylsulfonyl-myo-*inositol* (***14***). A mixture of **10** (500 mg) and 80% aqueous acetic acid (25 m*l*) was refluxed for 2 hr and then evaporated to dryness. Tlc showed two spots together with a trace of **14**. The residue was digested with ethanol-pyridine to give a crude mixture (292 mg), mp 125—145°C. A 100 mg-portion of the mixture was acetylated with acetic anhydride (1 m*l*) and pyridine (1 m*l*) at 85°C for 1 hr and the solution was evaporated to dryness. Crystallization from chloroform-ethanol gave crystals (102 mg, 59%) of **14**, mp 174—177.5°C. An analytical sample recrystallized showed the same melting point. PMR ($CDCl_3$): τ 7.56 (6, s, 2OTs C-CH_3), 7.77 (3, s, OTs C-CH_3), 7.85, 8.16 (3, s, OAc).

Found: C, 54.81; H, 4.55; S, 11.46%. Calcd for $C_{38}H_{38}O_{15}S_3$: C, 54.93; H, 4.61; S, 11.58%.

p-*Toluenesulfonylation of* ***3a***. *Preparation of 3,6-di-O-benzoyl-1,2-O-cyclohexylidene-5-O-p-tolylsulfonyl*-myo-*inositol* (***15a***) *and 3,6-di-O-benzoyl-1,2-O-cyclohexylidene-4,5-di-O-p-tolylsulfonyl*-myo-*inositol* (***16***). a) To a solution of **3a** (1.00 g) in dry pyridine (12 m*l*) was added, under ice cooling, 7 equiv. of *p*-toluenesulfonyl chloride (2.85 g) and the reaction mixture was allowed to stand at room temperature for 3 days. The mixture was then poured into water and the resulting crystals were collected. The crude mixture weighed 1.10 g, its tlc showing three components. Recrystallization of the crude mixture from chloroform gave thin needles (378 mg, mp 201—203°C) of **16**. An analytically pure sample of **16** was obtained by recrystallization from chloroform-ethanol: plates (335 mg, 20.2%), mp 203—205°C. From the mother liquor of crude **16**, by crystallization from chloroform, practically pure crystals (238 mg) of **15a**, and a mixture of **15a** and **16** (181 mg) were obtained. Further recrystallization from chloroform-ethanol afforded prisms (162 mg, 12%) of **15a**, mp 196—198°C.

15a: Found: C, 63.13; H, 5.39; S, 5.46%. Calcd for $C_{33}H_{34}O_{10}S$: C, 63.65; H, 5.50; S, 5.15%.

16: Found: C, 61.83; H, 5.27; S, 8.35%. Calcd for $C_{40}H_{40}O_{12}S_2$: C, 61.83; H, 5.19; H, 8.26%.

b) Compound **3a** (1.00 g) was treated with 3 equiv. of *p*-toluenesulfonyl chloride (1.22 g) in dry pyridine (10 m*l*) at room temperature for 2 days. The reaction mixture was processed as in (a) to give crude crystals which were recrystallized from chloroform-ethanol, giving pure crystals (413 mg, 31%) mp 196.5—198.5°C. By tlc, it was shown to be contaminated with a trace of **16**.

A 50 mg-portion of the compound was acetylated as in the preparation of **14** to give crystals (50 mg, 94%) of the acetate (**15b**) mp 194—197°C. Recrystallization from chloroform-ethanol afforded an analytical sample, mp 197.5—199.5°C.

Found: C, 62.84; H, 5.25; S, 5.41%. Calcd for $C_{35}H_{36}O_{11}S$: C, 63.24; H, 5.46; S, 4.82%.

1-O-Benzoyl-5-chloro-5-deoxy-4,6-di-O-p-tolylsulfonyl-neo-*inositol* (***17a***). A mixture of **11** (0.50 g) and 80% aqueous acetic acid (25 ml) was refluxed for 100 min, and the mixture was evaporated to dryness to give a crystalline residue. It was recrystallized from ethanol to give colorless rods (351 mg, 80%) of **17a**, mp 186—188°C. Recrystallization from ethanol afforded an analytical sample with the same melting point.

Found: C, 53.12; H, 4.44%. Calcd for $C_{27}H_{27}O_{10}S_2Cl$: C, 53.07; H, 4.45%.

1,2-Di-O-acetyl-3-O-benzoyl-5-chloro-5-deoxy-4,6-di-O-p-tolylsulfonyl-neo-*inositol* (***17b***). Compound **17a** (190 mg) was acetylated as in the preparation of **12b** to give crystals (223 mg, 100%) of **17b**, mp 197—203°C. Recrystallization from chloroform-ethanol gave an analytical sample, mp 198—200°C. PMR ($CDCl_3$): τ 5.20 (1, t, H-5, J=3.0 Hz), 7.51, 7.64 (3, s, OTs C-CH_3), 7.88, 8.14 (3, s, OAc).

Found: C, 53.21; H, 4.33%. Calcd for $C_{31}H_{31}O_{12}S_2Cl$: C, 53.54; H, 4.50%.

Reaction of ***10*** *with Pyridine Hydrochloride.* A mixture

of **10** (1.04 g) and pyridine hydrochloride (1.20 g) was heated in a sealed tube at 105—110°C for 45 hr. The brown mixture was then poured into water and the resulting oily product was extracted with chloroform. The extract was washed successively with 10% aqueous sodium carbonate, N hydrochloric acid and water, and dried over anhydrous sodium sulfate. Evaporation of the solution gave an oily product which was crystallized from ethanol to afford a mixture of **10** and **11** (100 mg), and **11** (34.5 mg, 3.9%), mp 182—183°C.

Compound **8a** was subjected to the same reaction condition as described above, but, no formation of **11** could be observed.

p-*Toluenesulfonylation of* ***1a*** *at Elevated Temperature. Preparation of 1,2-*O*-Cyclohexylidene-3,4,5,6-tetra-*O*-p-tolylsulfonyl-myo-inositol (****18****) and 5-Chloro-1,2-*O*-cyclohexylidene-5-deoxy-3,4,6-tri-*O*-p-tolylsulfonyl-neo-inosotol (****19****).* To a solution of **1a** (10.0 g) in dry pyridine (100 m*l*) was added *p*-toluenesulfonyl chloride (51 g, 7 equiv.), and the mixture was kept at room temperature for 2 days and then at 90—95°C for 10 hr. The mixture was then poured into ice and water and the resulting oily product crystallized gradually. The precipitates were dissolved in chloroform (100 m*l*) and the solution was washed successively with 10% aqueous sodium carbonate, N hydrochloric acid and water, and dried over anhydrous sodium sulfate. Removal of the solvent gave an oily product which was crystallized from chloroform–ethanol to give crystals (3.9 g, 12%) of **19**, mp 175—179°C. Recrystallization from the same solvent afforded an analytical sample, mp 182—183.5°C. PMR ($CDCl_3$): τ 7.54 (9, s, OTs C–CH_3).

Found: C, 53.68; H, 5.30%. Calcd for $C_{33}H_{37}O_{11}S_3Cl$: C, 53.45; H, 5.00%.

From the mother liquor of **19**, **18** (9.4 g, 28%) was obtained by crystallization from ethanol and methyl ethyl ketone. Recrystallization from the same solvent gave an analytical sample, mp 127.5—130.5°C.

Found: C, 55.22; H, 5.20; S, 14.66%. Calcd for $C_{40}H_{44}O_{14}S_4$: C, 54.78; H, 5.06; S, 14.62%.

*2-Chloro-2-deoxy-1,3,4-tri-*O*-p-tolylsulfonyl-neo-inositol (****20a****).* A mixture of **19** (535 mg) and 80% aqueous acetic acid (20 m*l*) was refluxed for 2 hr and then evaporated to dryness. The residue was recrystallized from ethanol to give crystals (462 mg, 96%) of **20a**, mp 187—188°C. Recrystallization from ethanol–methyl ethyl ketone gave an analytical sample mp 187—189°C.

Found: C, 49.32; H, 4.39%. Calcd for $C_{27}H_{29}O_{11}S_3Cl$: C, 49.04; H, 4.42%.

*1,2-Di-*O*-acetyl-5-chloro-5-deoxy-3,4,6-tri-*O*-p-tolylsulfonyl-neo-inositol (****20b****).* Crude **20a** obtained from **19** (0.53 g) by the above procedure was acetylated with acetic anhydride (5 m*l*) and pyridine (10 m*l*) overnight at room temperature. Evaporation of excess reagent gave an oily product which was crystallized from ethanol to afford needles (0.52 g, 100%) of **20b**, mp 149—152°C. Recrystallization from ethanol–methyl ethyl ketone gave plates or needles (0.17 g, 35%), mp 175—176°C (after sintering at 150°C. PMR ($CDCl_3$): τ 7.53 (6, s, OTs C–CH_3), 7.57 (3, s, OTs C–CH_3), 7.88, 8.14 (3, s, OAc).

Found: C, 50.24; H, 4.57%. Calcd for $C_{31}H_{33}O_{13}S_3Cl$: C, 50.05; H, 4.44%.

*4,5-Di-*O*-benzoyl-1,2-*O*-cyclohexylidene-3,6-di-*O*-p-tolylsulfonyl-myo-inositol (****21****).* To a solution of 1,2-*O*-cyclohexylidene-3,6-di-*O*-*p*-tolylsulfonyl-*myo*-inositol[1] (200 mg) in dry pyridine (2 m*l*) was added benzoyl chloride (0.16 m*l*, 4 equiv.) under ice cooling and the solution was allowed to stand in a refrigerator overnight. The mixture was then poured into water and the resulting crystals (289 mg) were recrystallized from chloroform–ethanol to give pure needles (266 mg, 97%) of **21**, mp 217—218°C.

Found: C, 62.02; H, 5.08; S, 8.28%. Calcd for $C_{40}H_{40}O_{12}S_2$: C, 61.83; H, 5.19; S, 8.26%.

*4,6-Di-*O*-benzoyl-1,2-*O*-cyclohexylidene-3,5-di-*O*-p-tolylsulfonyl-myo-inositol (****22****).* 1,2-*O*-Cyclohexylidene-3,5-di-*O*-*p*-tolylsulfonyl-*myo*-inositol[1] (203 mg) was similarly treated with benzoyl chloride (0.20 m*l*, 5 equiv.) to give needles (228 mg, 82%) of **22**, mp 212—214°C. Recrystallization from chloroform–ethanol gave an analytical sample, mp 216—216.5°C.

Found: C, 62.12; H, 5.07; S, 8.03%. Calcd for $C_{40}H_{40}O_{12}S_2$: C, 61.83; H, 5.19; S, 8.26%.

*5,6-Di-*O*-benzoyl-1,2-*O*-cyclohexylidene-3,4-di-*O*-p-tolylsulfonyl-myo-inositol (****23****).* 1,2-*O*-Cyclohexylidene-3,4-di-*O*-*p*-tolylsulfonyl-*myo*-inositol[1] (200 mg) was treated with benzoyl chloride (0.16 m*l*, 4 equiv.) in the same way described for **21** to give needles (218 mg, 81%) of **23**, mp 152—154°C. An analytical sample was obtained by recrystallization from chloroform–ethanol, mp 153—154°C.

Found: C, 62.18; H, 5.12; S, 8.35%. Calcd for $C_{40}H_{40}O_{12}S_2$: C, 61.83; H, 5.19; S, 8.26%.

*4,5,6-Tri-*O*-benzoyl-1,2-*O*-cyclohexylidene-3-*O*-p-tolylsulfonyl-myo-inositol (****24****).* 1,2-*O*-Cyclohexylidene-3-*O*-*p*-tolylsulfonyl-*myo*-inositol[1] (1.00 g) was treated with benzoyl chloride (1.13 m*l*, 4 equiv.) in a refrigerator for 3 days. The reaction mixture was treated in the same way as for **21** to give crystals (1.61 g, 92%) of **24**, mp 198—200°C. Recrystallization from chloroform–ethanol gave an analytical sample with the same melting point.

Found: C, 66.82; H, 5.52; S, 3.96%. Calcd for $C_{40}H_{38}O_{11}S$: C, 66.11; H, 5.27; S, 4.41%.

The authors are grateful to Professor Sumio Umezawa for his kind advice, and to Mr. Saburo Nakada for carrying out the elementary analyses. Financial support from the Ministry of Education for this work is gratefully acknowledged.