Inositol Derivatives. 9. Lithium Aluminum Hydride Reduction of Inositol Epoxides and Their Sulfonates[1]

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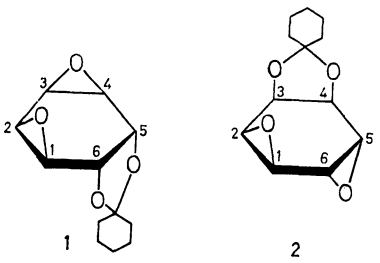
The reduction of two dianhydroinositols: 1,2:3,4-dianhydro-5,6-*O*-cyclohexylidene-*allo*-inositol (**1**) and 1,2: 5,6-dianhydro-3,4-*O*-cyclohexylidene-*allo*-inositol (**2**), and four sulfonylated anhydroinositols: 1,2-anhydro-5,6-*O*-cyclohexylidene-3,4-di-*O*-mesyl-*chiro*-inositol (**5b**), 1,2-anhydro-5,6-*O*-cyclohexylidene-3,4-di-*O*-tosyl-*chiro*-inositol (**5c**), 1,2-anhydro-5,6-*O*-cyclohexylidene-4-*O*-tosyl-*neo*-inositol (**6**) and 2,3-anhydro-4,5-*O*-cyclohexylidene-1,6-di-*O*-mesyl-*epi*-inositol (**8**), with lithium aluminum hydride has been investigated.

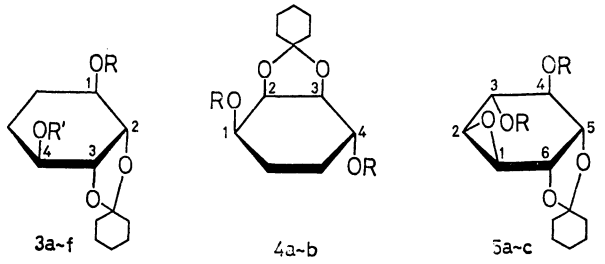
During a course of synthetic studies on deoxy- and dideoxy-inosadiamines,[2] it became necessary to prepare deoxy- and dideoxy-inositol derivatives. The reductive ring opening of an epoxide in sugars with lithium aluminum hydride ($LiAlH_4$) is an extensively studied reaction[3] which has been often used in a synthesis of deoxy-sugars.[4] However, few works have been done on the $LiAlH_4$ reduction of inositol epoxides.

$LiAlH_4$ reduction of 1,2-anhydro-5,6-*O*-cyclohexylidene-*chiro*-inositol (**5a**)[5] has been described to proceed regioselectively to give the 2-deoxy derivative in 87% yield,[6] and it has been suggested that the remote position in the epoxide from the *O*-cyclohexylidene group was preferentially attacked by the hydride. In the present study, the $LiAlH_4$ reduction of dianhydroinositol and sulfonyl derivatives of anhydroinositols have been attempted.

1,2: 3,4-Dianhydro-5,6-*O*-cyclohexylidene-*allo*-inositol (**1**)[5] was treated with $LiAlH_4$ in refluxing tetrahydrofuran (THF) to give a product (**3a**) in 54% yield, whose structure was established as 2,3-*O*-cyclohexylidene-1,4/2,3-cyclohexanetetrol on the basis of the following results.



Scheme 1.



	R	R′
a	H	H
b	Ms	H
c	Ms	Ac
d	Ms	Ms
e	Ts	H
f	Ts	

a	R=H
b	R=Ms

a	R=H
b	R=Ms
c	R=Ts

Scheme 2.

Reduction of 1,2: 5,6-dianhydro-3,4-*O*-cyclohexylidene-*allo*-inositol (**2**)[5] with $LiAlH_4$ at room temperature gave predominantly 2,3-*O*-cyclohexylidene-1,2,3/4-cyclohexanetetrol (**4a**) in 66% yield. Compound **4a** was characterized by converting it into the dimesyl derivative (**4b**), which revealed two sets of quartets at τ 5.43 and 5.79 in its PMR spectrum. These signals are attributed to the H-2 and H-3 protons and the stereochemistry between C-1 and C-4 has been established as *trans*.

In general, $LiAlH_4$ reduction of a secondary sulfonyloxy group of pyranose causes desulfonylation or desulfonyloxylation to give rise to a corresponding hydroxyl or deoxy derivative. Therefore, 1,2-anhydro-5,6-*O*-cyclohexylidene-3,4-di-*O*-sulfonyl-*chiro*-inositol (**5b**: dimesylate[7] and **5c**: ditosylate[5]) were subjected to the $LiAlH_4$ reduction.

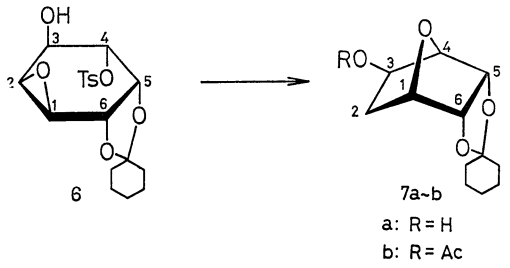
Reduction of **5b** at room temperature gave exclusively 2,3-*O*-cyclohexylidene-1-*O*-mesyl-1,4/2,3-cyclohexanetetrol (**3b**) in 70% yield, which was further converted to the acetyl (**3c**) and dimesyl derivatives (**3d**). The PMR spectrum of **3d** revealed a symmetrical multiplet (the A_2 part of the A_2X_2 system) due to the H-2 and H-3 protons at τ 5.62, which indicated a 1,4-*cis* arrangement of two mesyloxy groups, and thus the structure of **3d** was established. When the reduction was carried out at reflux temperature, **3a** was obtained predominantly in 50% yield. It was observed by tlc analysis that **3b** was formed initially in an earlier stage of the reaction and **3b** was subsequently converted into **3a** by further desulfonylation. The structure of **3a** was tentatively established by this fact.

Under the similar condition at reflux temperature, **5c** gave a monotosyl compound (**3e**) in 64% yield. It was shown that the tosyl group was less susceptible to the reduction than the mesyl group.

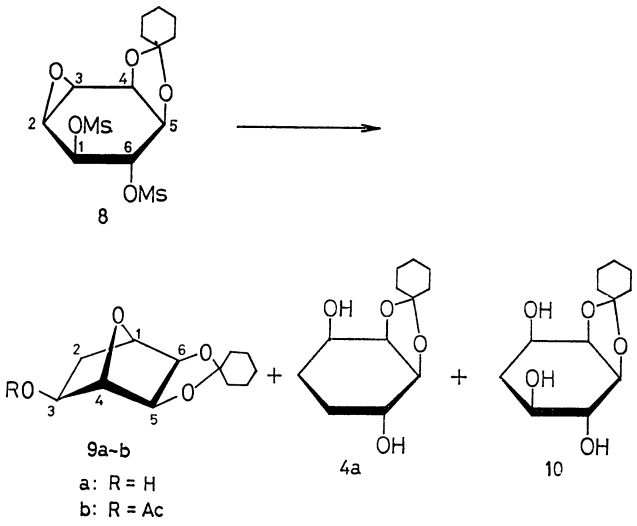
The reaction mechanism of these reductions might be explained as follows: Initially the hydride attacks exclusively on C-2 as in the case of **5a**, leading to the 2-deoxy compound. Then, a neighboring group participation of the hydroxyl group at C-1, probably by way of alumino hydride complex,[3b,8] results in a removal of the sulfonyloxy group on C-3 by a rear-side attack of the hydride giving rise to the dideoxy compounds.

In the above four compounds, the reduction occurred at the remote points from the *O*-cyclohexylidene group and this might be a reflection of the steric effect of the *O*-cyclohexylidene group.[4c,9]

The reduction of 1,2-anhydro-5,6-*O*-cyclohexylidene-4-*O*-tosyl-*neo*-inositol (**6**)[5] and that of 2,3-anhydro-4,5-*O*-cyclohexylidene-1,6-di-*O*-mesyl-*epi*-inositol (**8**)[7] afforded 1,4-anhydro-5,6-*O*-cyclohexylidene-2-deoxy-*allo*-inositol (**7a**) and -*cis*-inositol (**9a**) in 53 and 17% yield respectively.



Scheme 3.



Scheme 4.

The structure of **7a** was deduced from the elementary analysis and PMR spectrum. The C-2 *endo* proton appeared as a quartet at τ 7.29, which was remarkably deshielded by the 5,6-*endo* cyclohexylidene group. Acetylation of **7a** gave the acetyl derivative (**7b**), whose PMR spectrum showed the double doublet due to C-3 *endo* proton at τ 4.56. The formation of **7a** is reasonably explained by a mechanism involving reductive opening of the 1,2-epoxide ring at C-2 in the initial step followed by a transannular nucleophilic substitution by the C-1 hydroxyl group on the C-4 tosyloxy group.[5,10]

The structure of **9a** was also established by the elementary analysis and the well resolved PMR spectrum along with that of its acetyl derivative (**9b**) (Table 1). The coupling constants were shown to be in accordance with those reported for the related compound, *i.e.*, 2,3,5-tri-*O*-acetyl-1,4-anhydro-(2*S*)-2-hydroxyquinate.[11] In the case of **9b**, the double doublet due to the C-3 *endo* proton was upshifted by 0.76 ppm in comparison with that of **7b**, suggesting the presence of the cyclohexylidene group in the *exo* orientation.

Table 1. PMR spectral data of 1,4-anhydro-5,6-*O*-cyclohexylidene-2-deoxy-*cis*-inositol (**9a**) and its acetyl derivative (**9b**) in $CDCl_3$ at 100 MHz

Compd	Chemical shifts[a]	
	9a	**9c**
H_1	5.53 d	5.53 dt
H_{2endo}	—	8.18 qd
H_{2exo}	—	—
H_3	6.15 dd	5.32 dd
H_4	5.73 s	5.62 s
H_5	5.88 d	5.82 d
H_6	5.82 d	5.73 d

Compd	Coupling constants[b]	
	9a	**9b**
$J_{1,2endo}$	0	1
$J_{1,2exo}$	5.5	5.2
$J_{2endo,3}$	6.3	6.8
$J_{2exo,3}$	2.8	3.2
$J_{3,4}$	0	0
$J_{4,5}$	0	0
$J_{5,6}$	5.5	5.5
$J_{1,6}$	0	1
J_{2gem}	—	−13.5

a) Measured on Varian HA-100D (100 MHz) spectrometer. Chemical shifts are given in terms of τ-values, the signals being denoted by s (singlet), d (doublet), dd (double doublet), dt (double triplet), and qd (quartet of doublet). b) Values given for coupling constants are of first-order.

In the case of the reduction of **8**, **9a**, **4a** and 4,5-*O*-cyclohexylidene-2-deoxy-*epi*-inositol (**10**) were obtained in 17, 4.5 and 11% yields, respectively, after fractionation by a column chromatography. The structure of **10** was confirmed by converting it to the known 2-deoxy-*epi*-inositol (**11a**) and its derivative (**11b**).[12] The hydride might attack predominantly on C-2 of **8** to give an intermediary 2-deoxy derivative, from which the three crystalline compounds thus identified are obtained without a big contradiction in a reaction mechanism. That is, desulfonylations of the intermediate afford **10**, and desulfonylation along with desulfonyloxylation gives **4a**. Desulfonylation on the C-1 mesyloxy group and transannular displacement of the C-6 mesyloxy group by the C-3 hydroxyl group yield **9a**.

Experimental

Melting points were determined on a Mitamura Riken micro hot stage and are uncorrected. IR spectra were measured on a JASCO IR-E spectrophotometer in KBr disks. PMR spectra were obtained on a Varian A-60D (60 MHz) spectrometer in deuteriochloroform solution with tetramethylsilane as an internal standard. Chemical shifts are given in terms of τ-values and signals are denoted by s (singlet), d (doublet), dd (double doublet), t (triplet), or m (complex multiplet). All the solutions were concentrated under reduced pressure at 40—50 °C. Tlc was performed on a silica gel plate (Wako-gel B-10, Wako Pure Chemical Industries, Ltd.).

$LiAlH_4$ Reduction of 1,2: 3,4-Dianhydro-5,6-O-cyclohexylidene-allo-inositol (1).[5] To a stirred slurry of $LiAlH_4$ (0.16 g, 3 mol equiv.) in THF (20 ml), was added slowly a solution of **1** (0.30 g) in THF (5 ml), and the reaction mixture was heated under reflux for 30 min. The aluminum complex was then decomposed by addition of water (1 ml). The precipitates were removed by filtration and the filtrate was evaporated to give a crystalline residue which was pulverized with ethanol–*n*-hexane (1: 1, v/v) yielding 0.17 g (54%) of 2,3-*O*-cyclohexylidene-1,4/2,3-cyclohexanetetrol (**3a**): mp 138—139 °C. A part of the product was recrystallized from chloroform–ethanol to give an analytically pure sample, mp 140 °C.

Found: C, 63.12; H, 8.62%. Calcd for $C_{12}H_{20}O_4$: C, 63.13; H, 8.83%.

$LiAlH_4$ Reduction of 1,2: 5,6-Dianhydro-3,4-O-cyclohexylidene-allo-inositol (2).[5] To a stirred slurry of $LiAlH_4$ (80 mg, 3 mol equiv.) in THF (10 ml), a solution of **2** (150 mg) in THF (5 ml) was added, and the agitation was continued for 21 hr at room temperature. The mixture was worked up as described for **1** to give 101 mg (66%) of 2,3-*O*-cyclohexylidene-1,2,3/4-cyclohexanetetrol (**4a**), mp 98—101 °C. A part of **4a** was recrystallized from ethyl acetate–*n*-hexane (1: 2, v/v) to give an analytically pure sample, mp 101—103 °C.

Found: C, 62.91; H, 8.71%. Calcd for $C_{12}H_{20}O_4$: C, 63.12; H, 8.83%.

2,3-O-Cyclohexylidene-1,4-di-O-mesyl-1,2,3,4-cyclohexanetetrol (4b). a) Compound **2** (0.50 g) was treated with $LiAlH_4$ (0.50 g) in THF (12 ml) as described above to give a crude product of **4a**, which was, without any purification, treated with mesyl chloride (0.80 g) in pyridine (5 ml) for 4 hr at room temperature. The reaction mixture was poured into ice-water to give a crystalline product. The product was recrystallized from ethanol to give 0.56 g (65%) of **4b**, mp 151.5—153.5 °C. PMR data: τ 5.43 (dd, 1, H-2, $J_{1,2}$ 3.5 Hz, $J_{2,3}$ 5.5 Hz), 5.79 (dd, 1, H-3, $J_{3,4}$ 6.5 Hz), 6.85 (s, 3, OMs) and 6.89 (s, 3, OMs).

Found: C, 43.62; H, 6.13; S, 16.82%. Calcd for $C_{14}H_{24}O_8S_2$: C, 43.73; H, 6.30; S, 16.68%.

b) A solution of **2** (1.0 g) in ethanol (40 ml) was hydrogenated in the presence of Raney nickel T-4[13] in a Parr shaker apparatus under 3.4 kg/cm^2 of hydrogen pressure for 43 hr at room temperature. The catalyst was filtered off and the filtrate was evaporated to dryness. The residue was treated with mesyl chloride as described in a) to give 1.05 g (61%) of **4b**, mp 152—153 °C. This compound was identical with that obtained in a).

1,2-Anhydro-5,6-O-cyclohexylidene-3,4-di-O-mesyl-chiro-inositol (5b). 1,2-Anhydro-5,6-*O*-cyclohexylidene-*chiro*-inositol (**5a**)[5] (1.5 g) was treated with mesyl chloride (2.9 ml) in pyridine (30 ml) in a refrigerator for 2 days, and then at room temperature for 2 days. The mixture was poured into ice-water and the resulting crystals were recrystallized from chloroform–ethanol (1: 1, v/v) to give 1.97 g (80%) of **5b**, mp 150—152 °C.

Found: C, 42.51; H, 5.54; S, 15.84%. Calcd for $C_{14}H_{22}O_9S_2$: C, 42.20; H, 5.57; S, 16.09%.

$LiAlH_4$ Reduction of 5b. A solution of **5b** (6.0 g) in THF (50 ml) was added dropwise to a stirred slurry of $LiAlH_4$ (1.8 g, 3 mol equiv.) in THF (250 ml), and the mixture was stirred at room temperature for 2.5 hr. The mixture was worked up as described in the reduction of **1** to give, after recrystallization from ethanol, 3.18 g (70%) of 2,3-*O*-cyclohexylidene-1-*O*-mesyl-1,4/2,3-cyclohexanetetrol (**3b**), mp 135—139 °C. A part of the product was recrystallized from ethanol to give an analytically pure sample, mp 139—141 °C.

Found: C, 51.10; H, 7.16; S, 10.28%. Calcd for $C_{13}H_{22}O_6S$: C, 50.96; H, 7.24; S, 10.46%.

Compound **3b** (0.20 g) was treated with acetic anhydride (5 ml) and pyridine (5 ml) overnight at room temperature. The solution was evaporated to give a syrup which was crystallized from ethanol to give 0.15 g (65%) of the acetyl derivative (**3c**), mp 90—93 °C. PMR data: τ 5.80 (the A_2 part of A_2X_2 system, 2, H-2 and H-3), 6.86 (s, 3, OMs) and 7.91 (s, 3, OAc).

Found: C, 52.08; H, 6.95; S, 9.35%. Calcd for $C_{15}H_{24}O_7S$: C, 51.71; H, 6.94; S, 9.20%.

Compound **3b** (2.6 g) was mesylated as described in **4b** to give, after recrystallization from chloroform–ethanol (1: 2, v/v), 2.8 g (86%) of the dimesyl derivative (**3d**), mp 169—170 °C. PMR data: τ 5.03 (m, 2, H-1 an H-4), 5.62 (the A_2 part of A_2X_2 system, 2, H-2 and H-3), 6.82 (s, 6, 2OMs), and 7.94 (t, 4, methylene protons on C-5 and C-6, J 3 Hz).

Found: C, 43.45; H, 6.27; S, 16.66%. Calcd for $C_{14}H_{24}O_8S_2$: C, 43.73; H, 6.30; S, 16.68%.

$LiAlH_4$ Reduction of 5a at Elevated Temperature. A solution of **5b** (1.0 g) in THF (40 ml) was treated with $LiAlH_4$ (0.70 g, 7 mol equiv.) at reflux temperature for 2.5 hr. The reaction mixture was worked up in the usual way to give 0.31 g (55%) of **3a**, mp 124—130 °C. A part of the product was recrystallized as described in **1** to give crystals of mp 140 °C which was identical with the compound **3a** obtained by the reduction of **1**.

$LiAlH_4$ Reduction of 1,2-Anhydro-5,6-O-cyclohexylidene-3,4-di-O-tosyl-chiro-inositol (5c).[5] A mixture of **5c** (8.0 g), $LiAlH_4$ (3.5 g, 6 mol equiv.) and THF (350 ml) was treated at reflux temperature for 1 hr. The reaction mixture was worked up as described in the preparation of **3b** to give, after recrystallization from ethanol, 3.54 g (64%) of 2,3-*O*-cyclohexylidene-1-*O*-tosyl-1,4/2,3-cyclohexanetetrol (**3e**), mp 136—139 °C. Recrystallization from ethanol afforded an analytically pure sample, mp 138—139 °C.

Found: C, 59.86; H, 6.82; S, 8.35%. Calcd for $C_{19}H_{27}O_6S$: C, 59.51; H, 7.09; S, 8.38%.

Conventional acetylation of **3e** (0.15 g) gave 0.12 g (70%) of the acetyl derivative (**3f**), mp 91—92 °C. PMR data: τ 5.88 (m, 2, H-2 and H-3), 7.54 (s, 3, aryl-CH_3) and 7.95 (s, 3, OAc).

Found: C, 59.29; H, 6.68; S, 7.72%. Calcd for $C_{21}H_{28}O_7S$: C, 59.42; H, 6.65; S, 7.55%.

$LiAlH_4$ Reduction of 1,2-Anhydro-5,6-O-cyclohexylidene-4-O-tosyl-neo-inositol (6).[5] To a slurry of $LiAlH_4$ (0.23 g, 3 mol equiv.) in THF (38 ml) was added a solution of **6** (0.80 g) in THF (6 ml), and the mixture was stirred for 6 hr at room temperature. The reaction mixture was worked up as described above to give a product, which showed in tlc (2-butanone–toluene 1: 1, v/v) a presence of one major component (R_f 0.51) and two minor components (R_f 0.33 and 0.29). The crude product was recrystallized from methanol to give 0.24 g (53%) of the major product: 1,4-anhydro-5,6-*O*-cyclohexylidene-2-deoxy-*allo*-inositol (**7a**), mp 77—80 °C. PMR data: τ 7.29 (dd, 1, H-2 *endo*, $J_{1,2endo}$ 0 Hz, J_{2gem} −13 Hz, $J_{2endo,3}$ 7.5 Hz).

Found: C, 63.85; H, 7.97%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

Conventional acetylation of **7a** (0.10 g) gave the acetyl derivative (**7b**), which was recrystallized from ethanol to give an analytically pure sample (70 mg, 59%), mp 88—89 °C. PMR data: τ 4.56 (dd, 1, H-3, $J_{2endo,3}$ 7.5 Hz, $J_{2exo,3}$ 2.5 Hz, $J_{3,4}$ 0 Hz), 7.21 (dd, 1, H-2endo, $J_{1,2endo}$ 0 Hz, J_{2gem} −13 Hz) and 7.94 (s, 3, OAc).

Found: C, 62.42; H, 7.37%. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51%.

The mother liquor from **7a** was concentrated to give a syrup which was chromatographed on a silica gel column (50 g) and eluted by 2-butanone–toluene (1: 1, v/v). From the fraction

of the two minor components, 4 mg of crystals, mp 130—131 °C were obtained by recrystallization from ethanol–*n*-hexane (1:2, v/v). This product was indistinguishable from **3a** on tlc, but the IR spectrum was somewhat different from that of **3a** to suggest that the product was probably an isomer of *O*-cyclohexylidene-cyclohexanetetrol.

*$LiAlH_4$ Reduction of 2,3-Anhydro-4,5-O-cyclohexylidene-1,6-di-O-mesyl-*epi*-inositol (8).*[7] Compound **8** (4.0 g) was treated with $LiAlH_4$ (1.52 g) in THF (150 ml) at reflux temperature for 2 hr. The mixture was worked up in the usual manner to give a syrupy product (1.8 g), whose tlc showed the presence of four components: R_f 0.46, 0.38, 0.32, and 0.18 (2-butanone–toluene 2:1, v/v). The product was chromatographed on a silica gel column (100 g) with 2-butanone–toluene (2:5, v/v) as an eluent.

First fraction gave 391 mg (17%) of 1,4-anhydro-5,6-*O*-cyclohexylidene-2-deoxy-*cis*-inositol (**9a**), mp 100 °C. Recrystallization from ethanol–*n*-hexane (1:2, v/v) gave an analytically pure sample, mp 98—101 °C.

Found: C, 63.60; H, 8.00%. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02%.

Compound **9a** was acetylated in the usual manner to give the acetyl derivative (**9b**), mp 88—90 °C. Recrystallization from ethanol–*n*-hexane (1:2, v/v) gave an analytical sample, mp 90—91 °C.

Found: C, 62.36; H, 7.40%. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51%.

Second fraction gave 103 mg (4.5%) of **4a**, mp 98—100 °C, which was identified with the compound obtained from **2**.

Third fraction gave a homogeneous syrup (0.20 g, 8.7%) which was shown by tlc and IR spectrum to be an isomer of *O*-cyclohexylidene-cyclohexanetetrol. But a further structural elucidation was not attempted.

Fourth fraction gave 283 mg (11%) of 4,5-*O*-cyclohexylidene-2-deoxy-*epi*-inositol (**10**), mp 129—133 °C. Recrystallization from ethyl acetate gave an analytically pure sample, mp 133—135 °C.

Found: C, 59.02; H, 8.42%. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25%.

Compound **10** (0.20 g) was hydrolyzed in 80% aqueous acetic acid to give, after recrystallization from aqueous methanol, 33 mg of 2-deoxy-*epi*-inositol (**11a**), mp 205—215 °C (lit.[12a] mp 208 °C). (Found: C, 43.66; H, 7.36%).

Conventional acetylation of **11a** (70 mg) gave, after recrystallization from chloroform–ethanol, 140 mg (88%) of the pentaacetyl derivative (**11b**), mp 124—125 °C (lit.[12] mp 113—114 °C, 123—124 °C). PMR data: τ 7.79 (s, 3, axial OAc), 7.94 (s, 3, equatorial OAc), 7.95 (s, 3, equatorial OAc), 7.98 (s, 3, equatorial OAc) and 7.99 (s, 3, equatorial OAc). (Found: C, 51.55; H, 6.02%).

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1) A part of this experiment was presented at the 30th Annual Meeting of the Chemical Society of Japan, Osaka, April 4, 1974 (Abstract of papers of the meeting, Vol. 3, p.1888). In this paper, all the compounds except for *meso*-compounds are racemic and the formulas depict one enantiomer of the racemate.

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