Steric and Electrostatic Effects on the Elimination of 2- and 3-Sulphonyloxy-groups from Methyl 4,6-*O*-Benzylidenehexopyranosides

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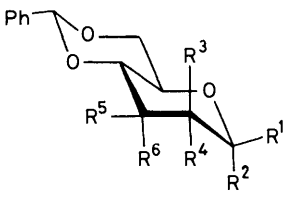
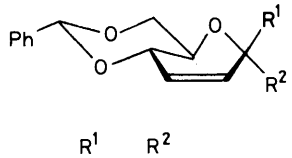
The elimination of 2- and 3-sulphonyloxy-groups from methyl 4,6-*O*-benzylidenehexopyranosides by the Tipson–Cohen reaction (sodium iodide–zinc in *NN*-dimethylformamide) has been studied. The β-glucoside 2,3-disulphonate (3) or (4) is rapidly changed into the 2,3-unsaturated sugar (8) in high yield, whereas the yield of 2-enoside (7) from the α-anomer (1) is only 55%. The α-mannoside sugar disulphonate (6) was converted into the unsaturated sugar (8) in 66% yield, whereas the β-isomer gave the enoside (7) in low yield. The differences in reactivity are discussed in the light of steric and electrostatic effects.

WE have reported previously[1] that the direct elimination of the 2- and 3-sulphonyloxy-groups from methyl 4,6-*O*-benzylidene-D-glucopyranosides by the Tipson–Cohen reaction [2] is strongly influenced by the anomeric configuration of the disulphonate. The β-2-enopyranoside (8) was obtained from the sulphonate (3) or (4) in high yield by brief heating under reflux, whereas the α-anomer (1) gave the unsaturated sugar (7) in lower yield even after a comparatively long reflux time. These observations and other work [3] on the synthesis of 2′,3′-unsaturated nucleosides by the Tipson–Cohen reaction prompted us to investigate the mechanism of this elimination reaction. No relevant evidence has yet been published except for a presumption [4] based on the elimination of terminal bis-*p*-tolylsulphonyloxy-groups with sodium iodide.[5]

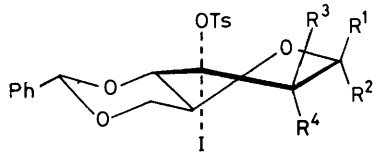
The substrates studied were the glucopyranosides (1),[6] (2),[7] (3),[8] and (4),[9] and the mannopyranosides (5) [10] and (6). Refluxing a suspension of the β-glucoside (3) in *NN*-dimethylformamide (DMF) with a 20-fold excess of sodium iodide and zinc dust [11] for 5 min led to the disappearance of the starting material and the formation of one



	R^1	R^2	R^3	R^4	R^5	R^6
(1)	H	OMe	H	OTs	OTs	H
(2)	H	OMe	H	OMs	OMs	H
(3)	OMe	H	H	OTs	OTs	H
(4)	OMe	H	H	OMs	OMs	H
(5)	H	OMe	OTs	H	OTs	H
(6)	OMe	H	OTs	H	OTs	H
(9)	H	OMe	H	OH	H	H
(10)	OMe	H	H	OTs	H	N_3
(12)	OMe	H	H	OTs	H	I
(14)	OMe	H	OTs	H	H	I
(16)	H	OMe	H	OTs	I	H
(17)	OMe	H	H	OTs	I	H



	R^1	R^2
(7)	H	OMe
(8)	OMe	H



	R^1	R^2	R^3	R^4
(11)	OMe	H	H	OTs
(13)	OMe	H	OTs	H
(15)	H	OMe	H	OTs

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product [t.l.c. in benzene–ethyl acetate (10 : 1)]. The unsaturated sugar (8) was obtained in 85% yield by direct crystallisation. Similar treatment of the methanesulphonate (4) gave the enoside (8) in 81% yield after refluxing for 30 min. When (3) was treated with only sodium iodide for 1 h in a similar manner, several unidentified spots were detected by t.l.c. in the same system. Furthermore, similar treatment of (3) with only zinc for 11 h gave no reaction.

Heating a suspension of the β-mannoside (6) in DMF with the Tipson–Cohen reagents under reflux for 2.5 h resulted in comparatively smooth elimination to give a single product (8) obtained in 66% yield by direct crystallisation. No other product was detected by t.l.c. during the reaction.

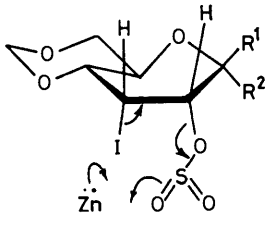
The same reagents in boiling DMF with the α-glucoside (1) for 12 h gave a mixture of the starting material and only one product (7), which was isolated in 55% yield (almost identical with that reported by Horton *et al.*[12]). Further, refluxing a suspension of (2) in DMF with the same reagents for 44 h gave a mixture showing four spots on t.l.c. in the same system. Silica gel column chromatography afforded, in order of elution, the unsaturated sugar (7) (13%), starting material (3%), the 3-deoxy-sugar (9) (9%), and an unidentified polar compound. Compound (9) was identified from m.p.[13] and ^{1}H n.m.r. spectra; [14] it is presumably formed by reductive cleavage of the starting material.

Reaction of the α-mannoside (5) with the same reagents under reflux in DMF for 15 h gave the unsaturated sugar (7) in 10% yield. When only sodium iodide was used as reagent, t.l.c. showed the presence of the starting material even after 15 h.

The above experiments indicate that these elimination reactions are strongly influenced by the anomeric configuration of the substrate. The first step of the elimination involves nucleophilic displacement of a sulphonyloxy-group by iodide ion. In the present experiments, iodo-intermediates were not detected by t.l.c., so such intermediates must be changed rapidly into unsaturated sugars.

To determine the position of initial attack by iodide ion, the β-gluco-compound (3) was treated with zinc and sodium azide instead of sodium iodide. Refluxing a suspension of (3) in DMF with a 20-fold excess of sodium azide for 30 min resulted in smooth displacement to give a single product (10) in 85% yield. Compound (10) was identified by ^{1}H and ^{13}C n.m.r. spectra. The H-3 signal occurred at higher field (*ca.* 0.5 p.p.m.) than that of (3), and the C-3 signal was also shifted to higher field (16 p.p.m.). Therefore initial attack by iodide ion must occur at C-3. In general, displacement of a 2-sulphonyloxy-group of a pyranose by a charged nucleophile seems to be more difficult than that of a 3-sulphonyloxy-group because of the electron-withdrawing inductive effect of the ring oxygen atom, an unfavourable alignment of dipoles, and electrostatic interactions in the transition state.[15]

Richardson has already described [16] two factors which seem to affect displacement at C-3 and -4 of pyranosides, namely the effect of a vicinal axial substituent and the β-*trans*-axial substituent effect. Since C-3 of the glucoside (3) has neither vicinal axial nor β-*trans*-axial substituents, dipole interaction and steric eclipsing effects in the transition state (11) for the displacement should be at a minimum. Further displacement with another iodide ion would seem to be impossible, in view of the rapid elimination rate of (3) or (4). DePuy *et al.* suggested [17] that the maximum elimination rate should be observed when the eliminated groups are disposed at a torsion angle of 0 or 180°. The β-*allo*-intermediate (12), owing to the orbital overlap of *p*-electrons between the C-2 and -3, can easily form a synperiplanar (dihedral angle 0°) system with a slight twist of the original chair conformation. Thus the Tipson–Cohen reaction of (3) occurs rapidly through displacement of the 3-sulphonyloxy-group by iodide ion and a convenient *cis*-elimination (Scheme 1).

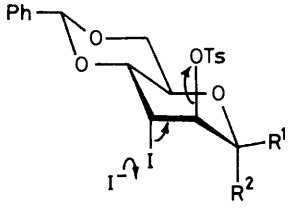


R^1 = OMe, R^2 = H or R^1 = H, R^2 = OMe

R = MePh or Me

SCHEME 1

As C-3 of the mannoside (6) has a vicinal axial substituent (2-sulphonyloxy-group), the eclipsing effect in the transition state (13) for the displacement should not be so small. However, once the β-*altro*-intermediate (14) is formed, an antiperiplanar system is present which can smoothly afford the unsaturated sugar (Scheme 2). This



R^1 = OMe, R^2 = H or R^1 = H, R^2 = OMe

SCHEME 2

could explain why the β-*manno*-sugar (6) reacts more slowly than the β-*gluco*-sugars (3) and (4).

[12] E. Albano, D. Horton, and T. Tsuchiya, *Carbohydrate Res.*, 1966, **2**, 349.
[13] B. Coxon, *Tetrahedron*, 1965, **21**, 3481.
[14] E. Vis and P. Karrer, *Helv. Chim. Acta*, 1954, **37**, 378.
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[17] C. H. DePuy, R. D. Thrun, and G. F. Morris, *J. Amer. Chem. Soc.*, 1962, **84**, 1314.

The 3-carbon atom of the α-*gluco*-sugar (1) or (2) has a β-*trans*-axial substituent (anomeric methoxy-group), and in the transition state (15) for the displacement, the eclipsing effect and dipole interaction should be at a maximum between the 1-methoxy- and 2-sulphonyloxy-groups. Therefore, the displacement will be slow.

In the case of the α-*manno*-sugar (5), C-3 has both a β-*trans*-axial substituent (anomeric methoxy-group) and a vicinal axial substituent (2-sulphonyloxy-group), so that the displacement at C-3 should be very slow, as observed.

To summarise, the following order of reactivity in the Tipson–Cohen reaction was obtained: β-*gluco* > β-*manno* > α-*gluco* > α-*manno*, and the reactivity of the substrate is controlled by the state of the first displacement at C-3 as described above; this step is rate-determining.

Newth has described [18] the quantitative conversion of the *gluco*-compound (16) into the enoside (7) by treatment with sodium iodide in acetone at 100 °C for 10 min. In the light of this fact, it might be suggested,† contrary to the above argument, that further displacement of the intermediate (12) by iodide ion could occur in the reaction of (3), and that *trans*-elimination of (17) formed by double displacement might occur smoothly. We therefore performed small-scale experiments under the same conditions as used in the azide substitution reaction of (3) (concentration of the starting material in DMF was decreased to one third as compared with the preparative-scale eliminations mentioned above) to define precisely the mechanism of enoside formation.

Treatment of the glucoside (3) with a 20-fold excess of sodium iodide and zinc in refluxing DMF for 40 min led to the disappearance of the starting material (t.l.c.) and gave a single product, characterised as the enoside (8). The same reaction with only sodium iodide for 15 min led to several products, along with unchanged starting material (t.l.c.). Reaction of the mannoside (6) with sodium iodide and zinc for 7 h led to the clean formation of the enoside (8). Although the reaction with only sodium iodide for 4 h led to the formation of (8) at the same rate as in the presence of zinc, further refluxing led to the decomposition of the product (8).

Reaction of the glucoside (3) with sodium azide in refluxing DMF for 30 min afforded the 3-azido-compound (10) as the sole product; addition of zinc to the reaction system produced no effect on the displacement rate. The same results were obtained in the displacement reaction of (3) with sodium benzoate.

Thus the displacement of a secondary sulphonyloxy-group by a charged nucleophile seems to be fast, contrary to our expectation, and zinc does not increase the rate of the reaction. In the preparative-scale experiments, the rate (5 min under reflux) of the reaction of (3) with the Tipson–Cohen reagents is therefore considered to be reasonable. Although we cannot exclude the possibility of double displacement by iodide ions, the *cis*-elimination mechanism might be expected in view of the facts that conversion of (3) into (8) occurs only in the presence of zinc and that conversion of (6) into (8) can proceed regardless of the presence of zinc.

† We thank a referee for this suggestion.

EXPERIMENTAL

N.m.r. data (solutions in deuteriochloroform; tetramethylsilane as internal standard) were recorded at 100 MHz with a JEOL PS-100 spectrometer. I.r. spectra were taken with a Hitachi EPI-G2 spectrometer. Mass spectra were obtained by direct insertion into the ion source of a Shimadzu LKB-9000 instrument.

Methyl 4,6,-*O*-benzylidene-α-D-glucopyranoside 2,3-bistoluene-*p*-sulphonate (1) was prepared from the corresponding diol by the method [6] of Richtmyer; m.p. 152—153°, $[\alpha]_D^{22}$ +13° (*c* 1.0 in chloroform) (lit., m.p. 147—148°). The 2,3-bismethanesulphonate (2) was prepared from the corresponding diol by the method [7] of Honeyman and Morgan; m.p. 187—188°, $[\alpha]_D^{22}$ +50° (*c* 1.0 in chloroform) (lit., m.p. 188—189°). Methyl 4,6-*O*-benzylidene-β-D-glucopyranoside 2,3-bistoluene-*p*-sulphonate (3) was prepared from the corresponding diol by the method [6] of Richtmyer; m.p. 159—160°, $[\alpha]_D^{22}$ −64° (*c* 1.0 in chloroform) (lit., m.p. 158°). The 2,3-bismethanesulphonate (4) was prepared by the method [9] of Guthrie *et al.*; m.p. 147—148°, $[\alpha]_D^{22}$ −62° (*c* 1.0 in chloroform) (lit., m.p. 148—149°).

Methyl 4,6-*O-Benzylidene*-2,3-*bis*-O-p-*tolylsulphonyl*-α-D-*mannopyranoside* (5).—Methyl 4,6-*O*-benzylidene-α-D-mannopyranoside [10] (560 mg, 2 mmol) and toluene-*p*-sulphonyl chloride (1.5 g, 8 mmol) dissolved in dry pyridine (10 ml) were heated at 95—100 °C with occasional stirring for 8 h. The mixture was poured into ice–water (300 ml). The *precipitate* in acetone (30 ml) was decolourised with charcoal and crystallised from acetone–ethanol; yield 600 mg (53%), m.p. 163—165°, $[\alpha]_D^{22}$ −12° (*c* 1.0 in chloroform) (Found: C, 56.7; H, 5.45. $C_{28}H_{30}O_{10}S_2$ requires C, 56.95; 5.1%).

Methyl 4,6-O-*Benzylidene*-2,3-*di*-O-p-*tolylsulphonyl*-β-D-*mannopyranoside* (6).—Methyl 2,3-*O*-isopropylidene-β-D-mannopyranoside [19] was converted into the 4,6-*O*-benzylidene derivative in fair yield. The benzylidene derivative (550 mg, 1.9 mmol) and toluene-*p*-sulphonyl chloride (1.45 g) in dry pyridine (30 ml) were heated at 90—100 °C overnight. The mixture was poured into ice–water (400 ml) and the precipitate was filtered off and crystallised from acetone–ethanol to give the *product* (6) (602 mg, 54%), m.p. 206—208°, $[\alpha]_D^{22}$ −92° (*c* 1.0 in chloroform) (Found: C, 56.7; H, 5.35. $C_{28}H_{30}O_{10}S_2$ requires C, 56.95; H, 5.1%).

Reactions of the 2,3-*Bis*-p-*toluenesulphonate* (1) *and the* 2,3-*Bismethanesulphonate* (2) *with Sodium Iodide and Zinc.*—A suspension of the glucoside (1) (2.8 g, 5 mmol), sodium iodide (15 g, 0.01 mol), and zinc (6.5 g, 0.1 mol) in DMF (70 ml) was refluxed for 12 h with stirring. After cooling, water (70 ml) was added and the mixture was extracted with chloroform (3 × 50 ml). The extracts were filtered, washed with water (30 ml × 2), dried (Na_2SO_4), and evaporated to a syrup. This was dissolved in ether and transferred to a column of silica gel (Wakogel C-300). Elution with benzene and benzene–ethyl acetate (20 : 1) gave *methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-α-D-gluco-*hex*-2-*enopyranoside* (7) (669 mg, 55%), m.p. 117—118.5°, $[\alpha]_D^{12}$ +120° (*c* 1.0 in chloroform), δ($CDCl_3$) 7.20—7.60 (5 H, m, ArH), 6.12 (1 H, d, $J_{2,3}$ 10 Hz, H-3), 5.70 (1 H, dt, $J_{2,3}$ 10 Hz, H-2), 5.56 (1 H, s, PhC*H*), 4.88 (1 H, m, H-1), 4.30 (1 H, m, H-4),

[18] F. H. Newth, *J. Chem. Soc.*, 1956, 471.
[19] P. J. Garegg, personal communication.

4.15 (1 H, m, H-5), 3.70—3.95 (2 H, m, H_2-6), and 3.42 (3 H, s, OMe) (Found: C, 67.8; H, 6.75. $C_{14}H_{16}O_4$ requires C, 67.75; H, 6.45%).

A similar reaction of the 2,3-bismethanesulphonate (2) (5.1 g, 0.01 mol) with the Tipson–Cohen reagents (20 equiv.) was performed for 44 h. After work-up as described above, the column was eluted with benzene and benzene–ethyl acetate (20 : 1 and 10 : 1) to give the unsaturated sugar (7) (420 mg, 13%), m.p. 116—118°, followed by starting material (150 mg) (identified by i.r. spectrum), and finally methyl 4,6-*O*-benzylidene-3-deoxy-α-D-glucoside (9) (300 mg, 9%), m.p. 184—185°, $[\alpha]_D^{23}$ +118° (*c* 0.41 in chloroform), i.r. bands for OH but no SO_2·OR, *m/e* 266 (M^+), δ($CDCl_3$) 7.2—7.5 (5 H, ArH), 5.48 (1 H, s, PhC*H*), 4.62 (1 H, d, $J_{1,2}$ 4.0 Hz, H-1), 4.22 (1 H, q, *J* 10 and 16 Hz, H-5), 3.4—3.9 (4 H, m, H-2 and -4, and H_2-6), 3.42 (3 H, s, OMe), and 1.5—2.2 (2 H, m, H_2-3).

Reactions of the 2,3-*Bistoluene*-p-*sulphonate* (3) *and the* 2,3-*Bismethanesulphonate* (4) *with Sodium Iodide and Zinc.*—A mixture of the glucoside (3) (1.0 g, 2 mmol), sodium iodide (6.0 g, 40 mmol), and zinc (2.6 g, 40 mmol) in dry DMF (30 ml) was refluxed for 5 min with stirring, then diluted with water (30 ml) and chloroform (50 ml), and filtered. The chloroform layer was separated and the aqueous layer extracted with chloroform (15 ml × 2). The combined extracts were washed with water (20 ml), dried (Na_2SO_4), and evaporated to a syrup, which crystallised directly from methanol to give *methyl* 4,6-*O*-*benzylidene*-2,3-*dideoxy*-β-D-gluco-*hex*-2-*enopyranoside* (8) (366 mg, 85%). The mother liquor still contained the product (8). A pure sample was obtained by recrystallisation from methanol; m.p. 94—95°, $[\alpha]_D^{12}$ +43° (*c* 1.0 in chloroform), δ($CDCl_3$) 7.20—7.60 (5 H, m, ArH), 6.15 (1 H, d, $J_{2,3}$ 10 Hz, H-3), 5.62 (1 H, d, $J_{2,3}$ 10 Hz, H-2), 5.58 (1 H, s, PhC*H*), 5.24 (1 H, m, H-1), 4.30 (1 H, m, H-4), 4.25 (1 H, m, H-5), 3.70—3.95 (2 H, m, H_2-6), and 3.42 (3 H, s, OMe) (Found: C, 67.8; H, 6.55. $C_{14}H_{16}O_4$ requires C, 67.75; H, 6.45%).

A similar reaction of the 2,3-bismethanesulphonate (4) (44 mg, 0.1 mmol) with sodium iodide (300 mg, 2 mmol) and zinc (130 mg, 2 mmol) in the same solvent (5 ml) was performed for 20 min. The crystalline product (20 mg, 81%) was identified as (8) by m.p. and i.r. spectrum.

Reaction of the 2,3-*Bistoluene*-p-*sulphonate* (5) *with Sodium Iodide and Zinc.*—A mixture of the disulphonate (5) (580 mg, 1 mmol), sodium iodide (3 g, 20 mmol), and zinc (1.3 g, 20 mmol) in dry DMF (15 ml) was treated in the usual manner for 15 h. The crystalline product, obtained in 10% yield, was identified as (7) by m.p. and i.r. spectrum.

Reaction of the 2,3-*Bistoluene*-p-*sulphonate* (6) *with Sodium Iodide and Zinc.*—A mixture of compound (6) (285 mg, 0.5 mmol), sodium iodide (1.5 g, 10 mmol), and zinc (650 mg, 10 mmol) in DMF (7 ml) was refluxed for 2.5 h with stirring. The unsaturated product (8) was crystallised directly from methanol [yield 80 mg (66%)] and its structure established by m.p. and i.r. spectrum.

Reaction of the Disulphonate (3) *with Sodium Azide.*—A mixture of compound (3) (576 mg, 1 mmol) and sodium azide (1.3 g, 20 mmol), in dry DMF (50 ml) was heated for 30 min at reflux with stirring. The cooled mixture was poured into ice–water (200 ml) and then extracted with ether (200 ml). The extract was washed with water, dried (Na_2SO_4), and evaporated to leave the crystalline product, *methyl* 3-*azido*-4,6-O-*benzylidene*-3-*deoxy*-2-O-p-*tolylsulphonyl*-β-D-*allopyranoside* (10) (390 mg, 85%). A sample recrystallised from methanol had m.p. 130—131°, $[\alpha]_D^{20}$ −78° (*c* 0.5 in chloroform), δ_H($CDCl_3$) 7.2—7.9 (9 H, m, ArH), 5.50 (1 H, s, PhCH), 4.58 (1 H, d, $J_{1,2}$ 7 Hz, H-1), 4.24—4.44 (3 H, m, H-2, 3, and -6), 3.56—4.04 (3 H, m, H-4, 5, and -6), 3.30 (3 H, s, OMe), and 2.44 (3 H, s, Ar*Me*); δ_C[$(CD_3)_2SO$] 98.6 (C-1), 75.9 (C-2), 61.3 (C-3), 76.2 (C-4), 63.5 (C-5), 67.8 (C-6), and 56.3 (OMe) (p.p.m. from tetramethylsilane) (Found: C, 54.5; H, 4.9; N, 9.15. $C_{21}H_{23}N_3O_7S$ requires C, 54.65; H, 5.0; N, 9.1%).

Reaction of the Disulphonate (3) *with Sodium Azide and Zinc.*—A mixture of compound (3) (576 mg, 1 mmol), sodium azide (1.3 g, 20 mmol), and zinc (1.3 g, 20 mmol) in DMF (50 ml) was refluxed for 30 min with stirring. By the same procedures as described above, crystals of (10) were obtained in 80% yield, identified by i.r. spectrum.

Reaction of the Disulphonate (3) *with Sodium Benzoate.*—A suspension of compound (3) (240 mg, 0.4 mmol) and sodium benzoate (60 mg, 0.42 mmol) in dry DMF (5 ml) was refluxed for 15 h with stirring. After cooling, water (15 ml) was added and the mixture was extracted with ethyl acetate (2 × 15 ml). The combined extract was washed with water, dried (Na_2SO_4), and evaporated to a syrup. *Methyl*-3-O-*benzoyl*-4,6-O-*benzylidene*-2-O-p-*tolylsuphonyl*-β-D-*allopyranoside* crystallised on addition of ether to the syrup, and was recrystallised from ether; yield 135 mg (61%), m.p. 175—176°, $[\alpha]_D^{20}$ −8° (*c* 0.5 in chloroform) (Found: C, 62.3; H, 5.25. $C_{28}H_{28}O_9S$ requires C, 62.2; H, 5.2%).

General Procedure for Small-scale Experiments.—A mixture of sulphonate (0.02 mmol) and sodium iodide (60 mg, 0.4 mmol) in dry DMF (1 ml) was refluxed for the appropriate time with stirring; the reaction was monitored by t.l.c. [benzene–ethyl acetate (10 : 1)]. Each reaction was also performed in the presence of zinc (0.4 mmol) under the same conditions.

We thank Dr. K. Ogura for discussions and Professor P. J. Garegg, Stockholm University, for details of the preparation of methyl β-D-mannopyranoside.

[6/1179 *Received*, 21*st June*, 1976]