Reductive Opening of Sugar Epoxides by Diborane-Borohydride Ion

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Carbohydrate epoxides were reduced selectively in the presence of sulfonyl ester, ketal, and acetal groups. Unlike more conventional reagents, such as aluminum hydride, alkoxyaluminum hydrides, and Raney nickel, this reagent permits the presence of a *trans*-(arylsulfonyl)oxy group adjacent to the epoxide ring. The regioselectivity of the ring-opening reaction appears to be controlled primarily by the steric and polar factors.

The reductive cleavage of the epoxide ring constitutes a useful method for the introduction of methylene and/or methyl group at various positions of carbohydrate derivatives.[1] In the course of work on some deoxy monosaccharides, we have faced a rather general synthetic problem of a selective reduction of an epoxide ring adjacent to a *trans*-(arylsulfonyl)oxy group. Usually ring opening with a hydride ion, as, for example, in lithium aluminum hydride reactions, can be expected to result in the displacement of the sulfonyloxy group with the formation of a new epoxide ring[1]. Raney nickel, which reductively cleaves epoxide rings, also reduces sulfonyloxy groups and leads to anhyride formation if an unsubstituted, sterically favorable hydroxyl group is available.[2]

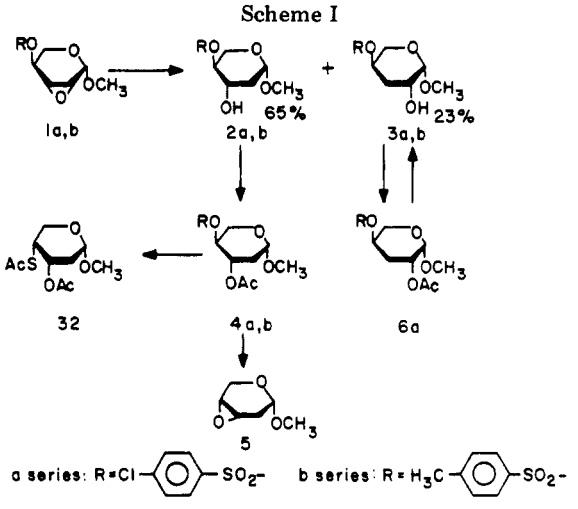
Diborane, an acid-type reducing agent,[3-6] has been shown to react rapidly with nonsugar epoxides in tetrahydrofuran in the presence of catalysts such as borohydride ion[4,7,8] or boron trifluoride[9] to produce alcohols. This reaction will proceed also without these catalysts but at a very slow rate.[5,7,9] Acetals, ketals, cyclic acetals, and cyclic ketals, which are the type of functions commonly present in carbohydrates, have also been reported to be reduced to ethers and hydroxy ethers by diborane in tetrahydrofuran.[10]

In this work, we have examined the diborane–borohydride reduction of the carbohydrate oxirane ring in the presence of sulfonyl ester, acetal, and ketal functions in an attempt to define the scope, limitations, and regioselectivity of this reaction.

Results

Reduction of the epoxide ring in methyl 2,3-anhydro-4-*O*-(*p*-toluenesulfonyl)-β-L-lyxopyranoside (**1b**, Scheme I) or in the corresponding 4-*O*-(*p*-chlorobenzenesulfonyl) derivative **1a** with diborane in tetrahydrofuran and in the presence of borohydride ion proceeds selectively and quantitatively without affecting the trans sulfonyl ester and acetal functions. Although the reductions of **1a** and **1b** proceed at room temperature, they are more advantageously carried out by heating the reaction mixture to reflux temperature, at which, in 1–2 days, a mixture of methyl 2-deoxy-4-*O*-(*p*-toluenesulfonyl)-β-L-*threo*-pentopyranoside (**2b**) and methyl 3-deoxy-4-*O*-(*p*-toluenesulfonyl)-β-L-*threo*-pentopyranoside (**3b**) and, in the case of **1b**, a mixture of (*p*-chlorobenzenesulfonyl) derivatives **2a** and **3a** is obtained. This reaction was applied successfully to the preparation of compounds **2a** and **2b** on a large scale (200 g). No products other than the 2-deoxy and 3-deoxy sugars (**2a,b** and **3a,b**) were detected by TLC. With either an excess of diborane or sodium borohydride, no reduction of **1a** or **1b** was achieved in 5 days at room temperature. Since it has been reported recently that carbohydrate nitro epoxides[11a] as well as some steroidal epoxides[11b] could be reduced by sodium borohydride in ethanol, reduction of **1b** with sodium borohydride in ethanol was next examined. At room temperature and with either an equimolar amount or a large excess of sodium borohydride, no reaction could be detected by TLC in 3 days. At 70 °C and in 2 days, TLC of the reaction mixture showed some starting material **1b** and a single spot of a product(s) with an R_f lower than that of either **2a** or **3a** to be present. The lack of UV absorption of this product(s) indicated that the tosyl group was cleaved, and, therefore, its structure was not investigated.

Scheme I



The positions of the deoxy functions in **2a,b** and **3a,b** were assigned on the basis of NMR spectra. The signals for the anomeric protons of the 2-deoxy derivatives (**2a,b**) appeared as pairs of doublets while those of the corresponding 3-deoxy derivatives were present as single doublets. Acetylation of **2a** and **3a** with acetic anhydride and pyridine gave monoacetylated products **4a** and **6a**, respectively. While treatment of **6a** with sodium methoxide in methanol effected simple deacetylation, compound **3a** being the only product formed, a similar treatment of

(1) Hanessian, S. *Adv. Carbohydr. Chem.* **1966**, *21*, 143.
(2) Kenner, G. W.; Murry, M. A. *J. Chem. Soc.* **1949**, S178.
(3) Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972.
(4) Brown, H. C.; Subba Rao, B. C. *J. Am. Chem. Soc.* **1960**, *82*, 681.
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(6) Brown, H. C.; Heim P.; Yoon, N. M. *J. Am. Chem. Soc.* **1970**, *92*, 1637.
(7) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1968**, *90*, 2686.
(8) Bessiere-Chretien, Y.; Meklati, B. *Tetrahedron Lett.*, **1971**, 621.
(9) Brown, H. C.; Yoon, N. M. *Chem. Commun.* **1968**, 1549.
(10) (a) Fleming, B.; Bolker, H. I. *Can. J. Chem.* **1974**, *52*, 888. (b) Bolker, H. I.; Fleming, B. I. *Ibid.* **1975**, *53*, 2818.
(11) (a) Baer, H. H.; Madumelu, C. B. *Carbohydr. Res.* **1975**, *39*, C8. (b) Weissenberg, M.; Krinsky, P.; Glotter, E. *J. Chem. Soc., Perkin Trans. 1* **1978**, 565.

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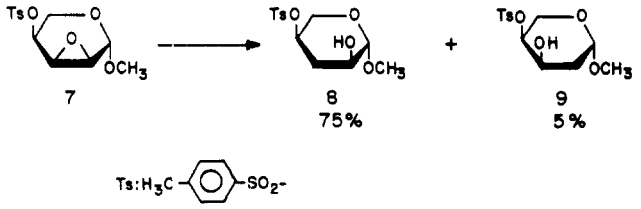
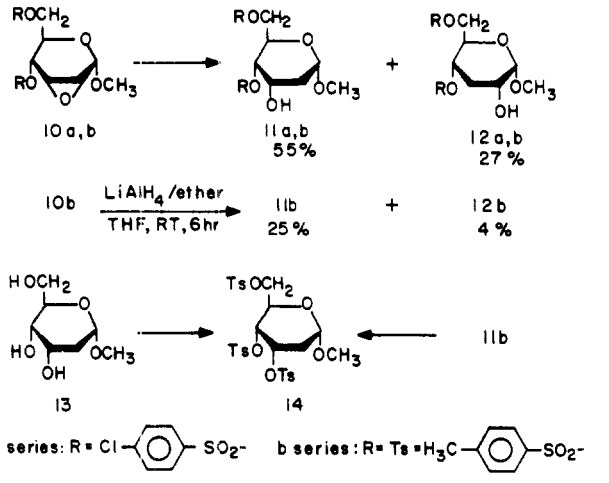
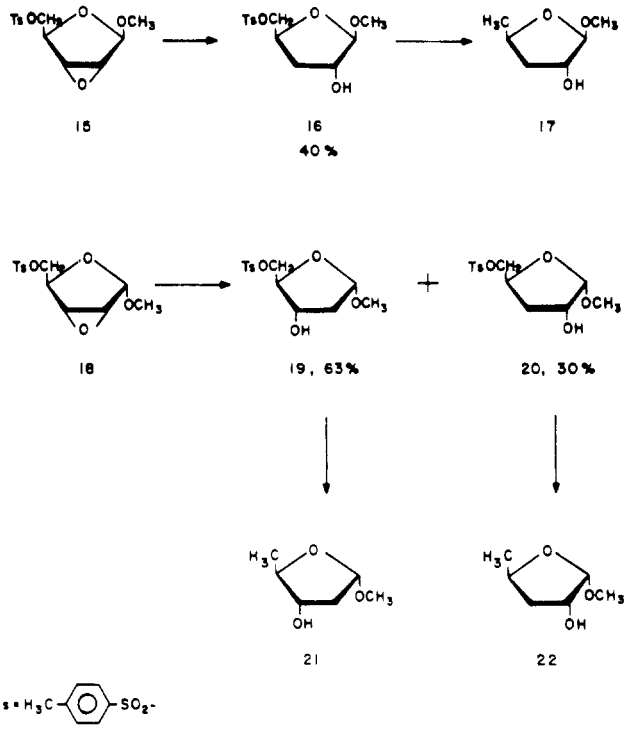
Scheme II



Scheme III



Scheme IV



4a resulted in the formation of a methyl 3,4-anhydro-2-deoxy-α-D-*erythro*-pentopyranoside (**5**, Scheme I). In addition, nucleophilic displacement of the sulfonyloxy group in **4a** with thioacetate anion in dimethylformamide (Scheme I) gave the known methyl 3-*O*-acetyl-4-*S*-acetyl-2-deoxy-4-thio-α-D-*erythro*-pentopyranoside[12] (**32**).

For comparison, compound **1b** was also subjected to reduction with lithium aluminum hydride in THF. After 2 h at room temperature and with an equimolar amount of $LiAlH_4$, TLC of the reaction mixture showed starting material **1b**, 2-deoxy sugar **2b**, and detosylated product (no UV absorption) in an approximately 1:1:2 ratio. Only a trace of the 3-deoxy derivative **3a** could be detected. When excess of $LiAlH_4$ was used, only the detosylated compound could be detected by TLC after 2 h.

To assess general applicability, we investigated additional examples of the diborane–sodium borohydride reduction of sulfonylated sugar epoxides.

Reduction of methyl 2,3-anhydro-4-*O*-(*p*-toluenesulfonyl)-β-L-ribopyranoside (**7**, Scheme II) gave methyl 3-deoxy-4-*O*-(*p*-toluenesulfonyl)-β-L-*erythro*-pentopyranoside (**8**) as the major product and a very small amount of the corresponding 2-deoxy derivative **9**. No other products were detected by TLC. The presence of a triplet for the anomeric proton of **8** and a doublet for that of **9** in the NMR spectra confirmed the positions of ring opening in the epoxide **7**.

Methyl 2,3-anhydro-4,6-bis[*O*-(*p*-toluenesulfonyl)]-α-D-allopyranoside (**10b**, Scheme III) was reported[13a] to be reduced by lithium aluminum hydride selectively at 18 °C to give a 47% yield of methyl 2-deoxy-4,6-bis[*O*-(*p*-toluenesulfonyl)]-α-D-allopyranoside **11b** and 43% recovered **10b**. Under more drastic conditions (1 h of reflux in tetrahydrofuran), the primary tosyloxy group was also reduced. Longer reaction time (several hours) led to the reduction of the epoxide ring and the primary tosyloxy group and removal of the secondary 4-*O*-tosyl group with the regeneration of a hydroxyl group.[13b] We have repeated the reduction of **10a** with $LiAlH_4$ under the mild conditions and found that in addition to the major 2-deoxy product **11b** a minor 3-deoxy derivative, **12b**, was formed, and some reduction (~10%) of the 6-*O*-tosyl group also occurred, when approximately 40% of **10b** had reacted.

In contrast, reduction of **10a,b** (Scheme III) with diborane–sodium borohydride gave a high yield of deoxy derivatives **11a,b** and **12a,b**, with no byproducts or starting material being detectable by TLC. The structural assignment of the 2-deoxy derivative **11b** was confirmed by its conversion to a tritosylate derivative, **14**, which was compared with an authentic compound prepared by tosylation of methyl 2-deoxy-α-D-allopyranoside.[14]

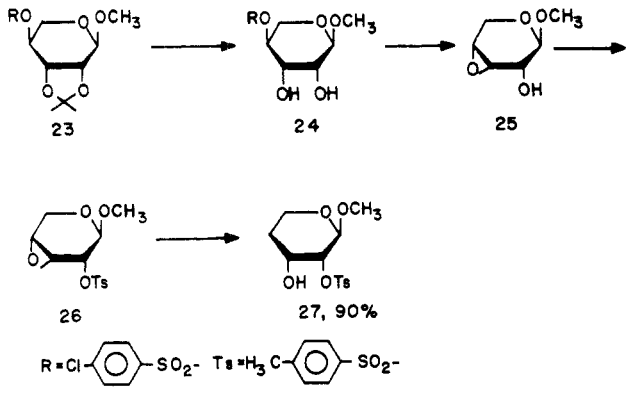
As an example of reduction of the oxirane ring fused to a furanose ring, the reduction of methyl 2,3-anhydro-5-*O*-(*p*-toluenesulfonyl)-D-ribofuranosides[15] **15** and **18** was investigated (Scheme IV). Lithium aluminum hydride reduction of the epoxide **15** has been shown by others[15] to furnish the 3-deoxy derivative **17** in low yield (~17%), and reduction[15] of the epoxide **18** gave a mixture of **21** and **22**, in a 68% total yield.

With diborane–sodium borohydride as the reducing agent, the reduction of **15** proceeded very slowly, furnishing a 40% yield of the 3-deoxy sugar **16** as the sole product. Approximately 50% of the starting material remained unreacted. The reduction of the α anomer **18**, under similar conditions, was considerably more easy, yielding a mixture (93%) of the deoxy sugars **19** and **20**. To prove the structures of **16**, **19**, and **20**, we reduced these compounds with lithium aluminum hydride to the known compounds[15] **17**, **21**, and **22**.

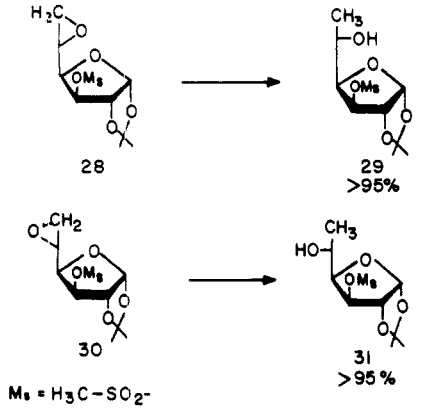
Reaction of methyl 3,4-anhydro-2-*O*-(*p*-toluenesulfonyl)-β-D-ribopyranoside (**26**) with diborane–sodium borohydride (Scheme V) proceeded with a high regioselectivity to furnish, in high yield (90%), the 4-deoxy derivative **27**. Only traces of a byproduct, presumably the corresponding 3-deoxy derivative, were detected by TLC.

(12) Fu, Y. L.; Bobek, M. *J. Org. Chem.* **1976**, *41*, 3831.
(13) (a) Bolliger, H. R.; Thürkauf, M. *Helv. Chim. Acta* **1952**, *35*, 1426. (b) Bolliger, H. R.; Ulrich, P. *Ibid.* **1952**, *35*, 93.
(14) Gut, M.; Prins, D. A. *Helv. Chim. Acta* **1947**, *30*, 1223.
(15) Goodman, L. *J. Am. Chem. Soc.* **1964**, *86*, 4167.

Scheme V



Scheme VI



The NMR spectrum of compound **27** (Table II, supplementary material) showed a doublet for the anomeric proton at δ 4.66, a triplet for H-2 at δ 4.5, and a doublet with each line further split into a doublet for H-5,5′, centered at δ 3.7, which was consistent with the structural assignment.

The terminal epoxides **28** and **30** were reduced very rapidly and selectively at room temperature by diborane–borohydride to give the secondary hydroxy derivatives **29** and **31** (Scheme VI). Under these conditions neither the methane sulfonyl nor the isopropylidene group was affected.

Discussion

The results obtained in this study are consistent with the suggested mechanism of diborane–sodium borohydride reduction of epoxides,[5] namely, that involving a Lewis acid assisted (BH_3) nucleophilic attack by sodium borohydride. As we have found, excess diborane effectively shields the sulfonyloxy function from a nucleophilic attack by a vicinal *trans*-hydroxy group. No appreciable difference in the course of reduction between the use of sodium and lithium borohydride was found.

Several articles[16-19] have discussed the various factors leading to regioselectivity in epoxide ring opening. Foremost among these are the steric, polar, and conformational effects.

The regiospecific reduction of the epoxides **28** and **30** can be explained primarily on steric and electronic grounds. The attack on the less hindered terminal carbon

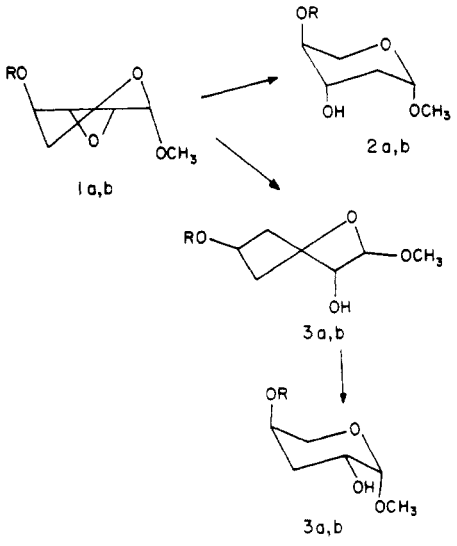


Figure 1.

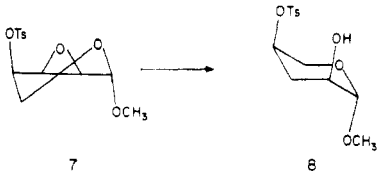


Figure 2.

is favored by the electronegative effects of the vicinal oxygen and, to a lesser degree, by the methanesulfonyloxy group.

The factors affecting the regioselectivity of epoxide ring opening become much more difficult to assess when that ring is fused to a flexible six-membered ring. Effects of the conformational factors on the regioselectivity may be predicted to some extent from a knowledge of the proportion of conformers in the ground state since many of the nonbonded interactions that determine the ratio of ground-state conformers are also present in the corresponding transition state.[20]

The proportion in which the two half-chair forms of methyl 2,3- and 3,4-anhydroaldopyranosides occur has been shown[21-23] to be determined by the anomeric effect and the tendency of the 4-(hydroxymethyl) or methyl group to assume the equatorial orientation. Because of the anomeric effect, compound **1** can be expected to assume predominantly a half-chair conformation in which the methoxy and sulfonyloxy groups are in a quasi-axial orientation (Figure 1). The quasi-axial orientation of these groups was indicated by a small coupling constant (~2 Hz) for the H-4 and H-5a protons. It is generally assumed[16,19] that diaxial opening of the epoxide ring leading to a chair conformer in the transition state is energetically favored over that leading to a "skew" form. Trans coplanar opening of the epoxide **1** at the 2-position would therefore lead to a *C*1 conformation product, **2**. This conformationally favored attack at the 2-position would, however, involve one unfavorable 1,3 interaction (and all axial substituents). An alternative trans coplanar opening of

(16) Buchanan, J. G.; Sable, H. Z. In "Selective Organic Transformations"; Thyagajaran, B. S., Ed.; Wiley-Interscience: New York, 1972; Vol. 2, p 1.
(17) Wohl, R. A. *Chimia* **1974**, *28*, 1.
(18) Pelter, A. *Chem. Ind. (London)* **1976**, 888.
(19) Kirk, D. N *Chem. Ind. (London)* **1973**, 109.
(20) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. In "Conformational Analysis"; Wiley: New York, 1965; p 358.
(21) Buss, D. H.; Hough, L.; Hall, L. D.; Mauville, J. F. *Tetrahedron* **1965**, *21*, 69.
(22) Buchanan, J. G.; Fletcher, R.; Parry, K.; Thomas, W. A. *J. Chem. Soc. B* **1969**, 377.
(23) Lemieux, R. V.; Watanabe, K. A.; Pavia, A. A. *Can J. Chem.* **1969**, *44*, 4413.

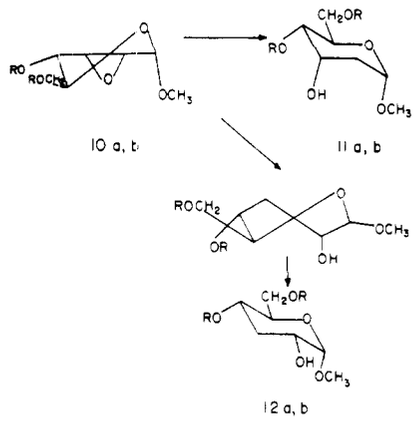


Figure 3.

the minor conformer of the epoxide 1 at C-3, involving an unfavorable anomeric effect, or attack at C-3 of the major conformer, involving a "skew"-like transition state, can therefore significantly compete with the attack at C-2. The electronic effects of the acetal function, which may be expected to be stronger than those of the 4-*O*-sulfonyl group, favor attack at C-3, and opposing this direction of opening is steric hindrance by a vicinal *trans*-sulfonyloxy group. The effects of the various factors are reflected in the ratio of the products **2** and **3** which is approximately 3:1. The fact that the 2-deoxy derivative is formed in a larger proportion may suggest that steric effects make a somewhat greater contribution than do the electronic and conformational factors.

Attack at C-3 of the epoxide **7** (Figure 2) with the formation of the product **8** is primarily favored by steric and by polar factors. The favorable effect of diaxial opening at C-3, leading to a *C*1 conformation, is somewhat diminished by one 1,3-diaxial interaction (and all axial substituents). The distribution of the products is therefore approximately 15:1 in favor of the 3-deoxy derivative **8**.

Reduction of the epoxide **10** at C-2, leading to *C*1 conformation product **11**, involves one unfavorable 1,3 interaction and a favorable disposition of the 1-methoxy, 4-sulfonyloxy, and bulky 5-(sulfonyloxy)methyl groups (Figure 3). Reduction at C-3 is favored by polar factors. The ratio of **11** to **12** (~2:1) suggests that conformational factors make a somewhat greater contribution than do the polar factors.

Regioselective opening of the epoxide **26** at C-4 is favored by polar factors. A competing attack at C-3, by diaxial opening, leading to a *C*1 conformation product in the transition state (Figure 4), involves one 1,3-diaxial interaction (all axial substituents) and a 1,3 interaction between the entering nucleophile and the methoxy substituent.

Because of the uncertainty of the conformational influences,[16] scission of the furanoid epoxides **15** and **18** can be rationalized only on the grounds of polar factors and steric hindrance.

Reduction of **15** proceeds extremely slowly and regioselectively at C-3, which may be accounted for by an opposing high steric hindrance by the C-1 and C-4 substituents and a destabilizing effect of the acetal function on the transition state having δ^+ at C-2. The relative importance of the steric factors as opposed to those of polar origin is further exemplified in the reduction of **18**. The product which is sterically favored is formed in a 2:1 ratio.

It is of interest to note that polar factors appear to assume a considerably larger importance for the regioselectivity of epoxide reduction by diborane–borohydride as compared to a reduction by lithium aluminum hydride.

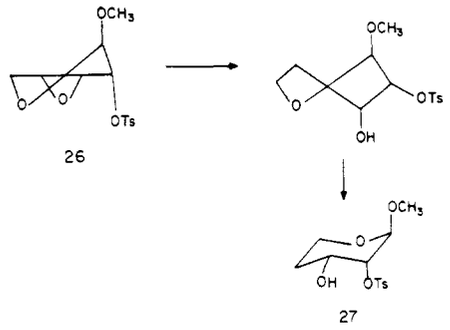


Figure 4.

Thus the product controlled by polar factors of the reduction of **18** is formed in a 1:2 ratio when diborane–borohydride is the reducing agent and only in a 1:9 ratio when lithium aluminum hydride is used.

Experimental Section

Melting points were determined on a Thermolyne No. MP-126000 melting point apparatus and are not corrected. The ^1H NMR spectra were recorded on a XL-100 spectrometer using Me_4Si as the internal standard. Optical rotation data were determined on a Perkin-Elmer 141 polarimeter. Solvents were removed under reduced pressure on a Buchler rotary evaporator. Thin-layer chromatography was performed on precoated plastic sheets (silica gel N-HR/UV_{254}, Brinkman Instruments, Inc.) in the following solvent systems: (A) benzene–acetone (9:1), (B) benzene–EtOAc (9:1). The spots were detected by UV absorbance or by spraying the sheets with 10% UV grade sulfuric acid–ethanol and heating. Column chromatography was done on silica gel (J. T. Baker No. 3405). Elemental analyses were performed by Robertson Laboratory.

Procedure for the Reduction of Sugar Epoxides with Diborane–Sodium Borohydride. To a solution of the epoxide (0.017 mol) in THF was added diborane in THF (20 mL of a 1 M solution containing 5 mol % of sodium borohydride) dropwise, and the solution was stirred at 70 °C (oil bath) under a current of dry nitrogen. After the starting material was no longer detectable by TLC, the reaction mixture was cooled to room temperature and hydrolyzed by addition of 10 mL of a 1:1 mixture of 1 M sulfuric acid and THF. Solid K_2CO_3 was added to neutralize the mixture followed by the addition of solid NaCl to saturate the aqueous phase. The mixture was extracted with ethyl ether and the ether solution was evaporated to a syrup. The syrup mixture was separated by chromatography on a dry silica gel column by using solvent system A or B as the eluant.

Procedure for *p*-Toluene- or *p*-Chlorobenzenesulfonylation of Sugar Alcohols. To a solution of the sugar alcohol (0.02 mol) in alcohol-free chloroform (10 mL) and dry pyridine (50 mL) was added a solution of *p*-toluene- or *p*-chlorobenzenesulfonyl chloride (0.04 mol) in alcohol-free chloroform (10 mL) and dry pyridine (100 mL), and the reaction mixture was stirred for 24 h. It was then poured into 500 mL of ice and water with stirring. The mixture was allowed to warm to room temperature, and it was extracted with chloroform (3 × 100 mL). The combined extracts were washed with cold hydrochloric acid, dilute sodium bicarbonate solution, and water. The solution was dried (Na_2SO_4) and evaporated to a syrupy or solid residue which was crystalized or purified by silica gel chromatography.

Methyl 2,3-anhydro-4-*O*-(*p*-chlorobenzenesulfonyl)-β-L-lyxopyranoside (1a) was prepared from methyl 2,3-anhydro-β-L-lyxopyranoside[12] by sulfonylation with *p*-chlorobenzenesulfonyl chloride.

Methyl 2,3-anhydro-4-*O*-(*p*-toluenesulfonyl)-β-L-lyxopyranoside (1b) was prepared from methyl 2,3-anhydro-β-L-lyxopyranoside[12] by sulfonylation with *p*-toluenesulfonyl chloride.

Methyl 3-*O*-acetyl-4-*O*-(*p*-chlorobenzenesulfonyl)-2-deoxy-β-L-*threo*-pentopyranoside (4a) was prepared from **2a** by acetylation with acetic anhydride in pyridine.

Methyl 2-*O*-acetyl-4-*O*-(*p*-chlorobenzenesulfonyl)-3-deoxy-β-L-*threo*-pentopyranoside (6a) was prepared from **3a**

by acetylation with acetic anhydride in pyridine.

Methyl 3-*O*-Acetyl-4-*S*-acetyl-2-deoxy-4-thio-α-D-*erythro*-pentopyranoside (32). Compound **4a** (3.65 g, 0.01 mol) was stirred with potassium thioacetate (3.5 g) in dry DMF (50 mL) at an oil-bath temperature of 95–100 °C under a current of dry nitrogen for 5 h. The reaction mixture was cooled to room temperature and poured with stirring into dry xylene (150 mL). The precipitated salts were filtered and washed with dry xylene. The combined filtrates were evaporated to a syrupy residue which was extracted with heptane (4 × 50 mL). The heptane solution was evaporated, and the syrupy residue was dissolved in dry pyridine (20 mL) and acetic anhydride (5 mL). After 16 h at room temperature, the reaction mixture was poured with stirring into ice–water (50 mL). The mixture was extracted with chloroform, and the extract was washed with water (2 × 10 mL), dried (Na_2SO_4), and evaporated to a syrup. Purification of this syrup by chromatography on silica gel, using solvent B as the eluant, gave **32** (52%) which was identical with an authentic sample of **32** prepared by a different procedure.[12]

Methyl 3,4-Anhydro-2-deoxy-α-D-*erythro*-pentopyranoside (5). Compound **4a** (3.65 g, 0.01 mol) was dissolved in a cold (0 °C) solution of sodium methoxide (300 mg of Na) in methanol (100 mL), and the reaction mixture was kept at 4 °C for 16 h. The mixture was evaporated and the residue extracted with ether. The ether solution was filtered and evaporated. Distillation of the residue at 0.005 mmHg and 35 °C gave pure **5**.

Methyl 2,3-Anhydro-4-*O*-(*p*-toluenesulfonyl)-β-L-ribopyranoside (7). Compound **7** was prepared by tosylation of methyl 2,3-anhydro-β-L-ribopyranoside.[23,24]

Methyl 2,3-anhydro-4,6-bis[*O*-(*p*-toluenesulfonyl)]-α-D-allopyranoside (10b) was prepared according to the reported procedure.[13b]

Methyl 2,3-anhydro-4,6-bis[*O*-(*p*-chlorobenzenesulfonyl)]-α-D-allopyranoside (10a) was prepared by *p*-chlorobenzenesulfonylation of methyl 2,3-anhydro-α-D-allopyranoside.[14]

Procedure for Lithium Aluminium Hydride Reductions. To a chilled (0 °C) stirred solution of lithium aluminum hydride in dry THF was added a solution of the compound dissolved in dry ether. The reaction mixture was stirred at room temperature, and the progress of the reduction was monitored by TLC. Wet ether was added cautiously to decompose the excess hydride, and the inorganic solids were filtered and washed with THF. The residue obtained by evaporation of the combined filtrates was separated by chromatography.

Methyl 4-*O*-(*p*-chlorobenzenesulfonyl)-2,3-*O*-isopropylidene-α-L-lyxopyranoside (23) was prepared by *p*-chlorobenzenesulfonylation of methyl 2,3-*O*-isopropylidene-α-L-lyxopyranoside.[25]

(24) Honeyman, J. *J. Chem. Soc. C* **1946**, 990.

Methyl 4-*O*-(*p*-Chlorobenzenesulfonyl)-α-L-lyxopyranoside (24). Compound **23** (30 g) was dissolved in 50% acetic acid (200 mL), and the solution was heated at 70 °C for 5 h. TLC of the reaction mixture showed only the presence of **24**. The solution was evaporated to a syrupy residue which was dissolved in toluene (400 mL). Evaporation of the toluene solution gave **24**.

Methyl 3,4-Anhydro-β-D-ribopyranoside (25). Compound **24** (33.9 g, 0.1 mol) was dissolved in a cold (0 °C) solution of sodium methoxide (3 g of Na) in methanol (500 mL), and the reaction mixture was kept at 4 °C for 24 h. The mixture was neutralized with methanolic HCl and evaporated, and the residue was extracted with CH_2Cl_2 (2 × 200 mL). The CH_2Cl_2 solution was filtered and evaporated to a syrup which was homogeneous by TLC.

Methyl 3,4-anhydro-2-*O*-(*p*-toluenesulfonyl)-β-D-ribopyranoside (26) was prepared by tosylation of 25.

5,6-Anhydro-1,2-*O*-isopropylidene-3-*O*-(methylsulfonyl)-β-L-idofuranose[26] (28) was prepared by the reported procedure.

5,6-Anhydro-1,2-*O*-isopropylidene-3-*O*-(methylsulfonyl)-α-glucofuranose[27] (30) was prepared according to the published method.

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Registry No. **1a**, 74128-31-7; **1b**, 74128-32-8; **2a**, 74128-33-9; **2b**, 74128-34-0; **3a**, 74128-35-1; **3b**, 74128-36-2; **4a**, 74128-37-3; **4b**, 74128-38-4; **5**, 74128-39-5; **6a**, 74128-40-8; **7**, 74128-41-9; **8**, 74128-42-0; **9**, 74128-43-1; **10a**, 74128-44-2; **10b**, 71811-64-8; **11a**, 74128-45-3; **11b**, 71811-67-1; **12a**, 74128-46-4; **12b**, 74128-47-5; **13**, 17676-18-5; **14**, 74128-48-6; **15**, 74128-49-7; **16**, 74128-50-0; **17**, 74128-51-1; **18**, 66108-06-3; **19**, 60134-27-2; **20**, 74128-52-2; **21**, 74128-53-3; **22**, 74128-54-4; **23**, 74128-55-5; **24**, 74128-56-6; **25**, 74128-57-7; **26**, 74128-58-8; **27**, 74128-59-9; **28**, 19286-05-6; **29**, 64243-86-3; **30**, 16848-30-9; **31**, 19235-24-6; **32**, 60295-31-0; methyl 2,3-anhydro-β-L-lyxopyranoside, 6207-00-7; methyl 2,3-anhydro-β-L-ribopyranoside, 56153-83-4; methyl 2,3-anhydro-α-D-allopyranoside, 3257-61-2; methyl 2,3-*O*-isopropylidene-α-L-lyxopyranoside, 2495-99-0.

Supplementary Material Available: Physical properties and analytical data (Table I) and selected ^1H NMR spectral parameters (Table II) for the new compounds (4 pages). Ordering information is given on any current masthead page.

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Mercury in Organic Chemistry. 18. Synthesis of Symmetrical Divinyl and Diaryl Ketones via Rhodium-Catalyzed Carbonylation of Vinyl- and Arylmercurials

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Vinylmercuric chlorides readily react with rhodium(I) and rhodium(III) catalysts and carbon monoxide to give excellent yields of divinyl ketones. The best reaction conditions are 0.5 mol % $[Rh(CO)_2Cl]_2$ and 2 equiv of lithium chloride under 1 atm of carbon monoxide at room temperature. This rhodium catalyst also provides improved yields of diaryl ketones from arylmercurials at 70 °C under 1000–1500 psi of carbon monoxide pressure. Organorhodium compounds are presumed to be intermediates in these reactions.

Divinyl ketones are employed in organic chemistry as double[1-8] and less frequently as single[9] Michael acceptors. Divinyl ketone equivalents have also been established as symmetrical or unsymmetrical double Michael accep-

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