SYNTHESES WITH ANHYDRO SUGARS. XVII.*

PREPARATION AND REACTIONS OF 1,6:2,3-DIANHYDRO-4-DEOXY- AND 1,6:3,4-DIANHYDRO-2-DEOXY-β-D-HEXOPYRANOSES WITH NUCLEOPHILIC AND REDUCING REAGENTS

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Reactions of the oxiran ring of 1,6:2,3-dianhydro-4-deoxy- and 1,6:3,4-dianhydro-2-deoxy-β-D-hexopyranoses (*I*—*IV*) with various reagents were investigated. 2-Deoxy- and 4-deoxyderivatives of dianhydrides of *ribo*-configuration *II* and *IV* react with 5% potassium hydroxide, magnesium iodide or methylmagnesium iodide, lithium aluminum hydride, and on atmospheric pressure catalytic hydrogenation on Raney nickel exclusively under diaxial splitting, while similar derivatives of *lyxo*-configuration, dianhydrides *I* and *III* give under the same conditions mixtures of products formed in addition to diaxial splitting also by diequatorial splitting. The results of these reactions in which diols, iodohydrins, and deoxy derivatives were formed were interpreted as a simultaneous effect of steric and polar influences on the splitting of the oxiran ring.

As yet undescribed 3,4-dideoxy-D-*erythro*- and 3,4-dideoxy-D-*threo*-hexopyranoses were obtained by hydrolysis or acetolysis of their 1,6-anhydro derivatives.

The method of opening of the oxiran ring of pyranoid sugar derivatives may be affected by the nature of the reagent, by steric effects, and also by polar effects. The steric and polar effects may be synergistic or antagonistic; in the first case the result is a highly selective — diaxial — splitting of the oxiran ring, while in the second it is a less selective splitting or even the formation of predominantly diequatorial products. In acyclic sugar derivatives, or in the case of cyclic, conformationally labile derivatives, the two effects can be separated only with difficulty. Therefore we considered it useful to investigate this problem on sterically rigid 1,6:2,3-dianhydro-4-deoxy- and 1,6:3,4-dianhydro-2-deoxy-β-D-hexopyranoses (*I*—*IV*), in which the oxiran ring is, from the point of view of polarity, substituted asymmetrically by the methylene group and the group containing oxygen atoms in the form of ether or acetal function. In this case a more pronounced influence of polar effects during the cleavage of the epoxide bonds may be expected than in the case of 1,6:2,3- and 1,6:3,4-dianhydro-β-D-hexopyranoses.

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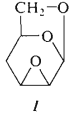
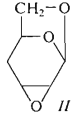
The starting 4-deoxydianhydro derivatives *I* and *II* were prepared by known procedures from 1,6-anhydro-4-deoxy-2-O-*p*-toluenesulfonyl-β-D-*xylo*-hexopyranose[1]: Dianhydro derivative *I* on reaction with sodium methoxide in methanolic chloroform[1], and dianhydro derivative *II* on reaction with methanesulfonyl chloride, by transforming it to 1,6-anhydro-4-deoxy-3-O-methanesulfonyl-2-O-*p*-toluenesulfonyl-β-D--*xylo*-hexopyranose and reacting the latter intermediate with sodium methoxide in methanol and tetrahydrofuran[2].

In the literature as yet undescribed 2-deoxydianhydro derivatives *III* and *IV** were prepared from 1,6:2,3-dianhydro-4-O-benzyl-β-D-manno-pyranose[4] (*V*). The latter compound was transformed to 1,6-anhydro-4-O-benzyl-2-deoxy-β-D-*arabino*--hexopyranose (*VI*) by lithium aluminum hydride reduction in tetrahydrofuran on one hand using a known procedure[5] (modified by us[2]), or on reaction of benzyl epoxide *V* with magnesium iodide in ether which led to 1,6-anhydro-4-O-benzyl--2-deoxy-2-iodo-β-D-glucopyranose (*VII*), and subsequent catalytic dehalogenation on Raney nickel on the other hand. Reaction of 2-deoxy derivative *VI* with *p*-toluenesulfonyl chloride in pyridine gave 3-O-tosyl derivative *VIII* which on debenzylation on palladium gave 1,6-anhydro-2-deoxy-3-O-*p*-toluenesulfonyl-β-D-*arabino*-hexopyranose (*IX*). This compound was submitted to reaction with sodium methoxide affording 1,6:3,4-dianhydro-2-deoxy-β-D-*ribo*-hexopyranose (*IV*). In a similar manner 1,6:3,4-dianhydro-2-deoxy-β-D-*lyxo*-hexopyranose (*III*) was also prepared. Acetylation of 2-deoxy derivative *VI* gave 3-O-acetyl derivative *X* which was debenzylated



I



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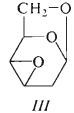
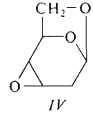
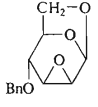


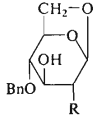
III



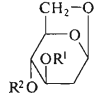
IV



V



VI, R=H
VII, R=I



VIII, R^1 = Ts, R^2 = Bn
IX, R^1 = Ts, R^2 = H
X, R^1 = $COCH_3$, R^2 = Bn
XI, R^1 = $COCH_3$, R^2 = H
XII, R^1 = $COCH_3$, R^2 = Ts
XIII, R^1 = H, R^2 = H

Ts = *p*-$CH_3C_6H_4SO_2$—
Bn = $C_6H_5CH_2$—

* While we carried out this work racemic forms of these compounds have been described[3].

catalytically to deoxy derivative *XI* and then transformed on reaction with *p*-toluenesulfonyl chloride to 3-O-acetyl-1,6-anhydro-2-deoxy-4-O-*p*-toluenesulfonyl-β-D-*arabino*-hexopyranose (*XII*). From the latter dianhydro derivative *III* was prepared on reaction with sodium methoxide in chloroform.

In further part of our work we investigated the reactions of dianhydro derivatives *I*–*IV* with aqueous potassium hydroxide solution, with magnesium iodide or methyl magnesium iodide in ether, with lithium aluminum hydride in tetrahydrofuran and under the conditions of catalytic reduction on Raney nickel T-1 (ref.[6]) in ethanol (Table I).

TABLE I

Products (yield in %) of the Reaction of 4-Deoxy-1,6:2,3- and 2-Deoxy-1,6:3,4-dianhydro-β-D--hexopyranoses

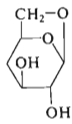
Dianhydro derivative (configuration)	5% KOH %	MgI_2 %	$LiAlH_4$ %	Raney Ni %	Course
4-Deoxy-	51, *XIV*	—	62·5, *XXI*	17, *XXI*	diax
-lyxo-(I)	49, *XV*	100, *XVII*	37·5, *XVIII*	74, *XVIII* 9, *XXXI*	dieq
4-Deoxy-	100, *XIV*	100, *XXII*	100, *XXIII*	96, *XXIII*	diax
-ribo-(II)	—	—	—	— 4, *XXXI*	dieq
2-Deoxy-	66, *XIII*[a]	90·5, *XX*[b]	76, *XXI*	60, *XXI*	diax
-lyxo-(III)	34, *XVI*	9·5, *XXV*	24, *XXVI*	31, *XXVI* 9, *XXXI*	dieq
2-Deoxy-	≈100, *XIII*[c]	100, *XXVII*	100, *XXVIII*	91, *XXVIII*[d]	diax
-ribo-(IV)	—	—	—	— 9, *XXXI*	dieq

[a] On the basis of optical rotation measurements the composition of the mixture was 64% (*XIII*) and 36% (*XVI*). [b] These values were obtained on analysis of the mixture of deoxy derivatives *XXI* and *XXVI* formed by reductive dehalogenation of iodohydrins. [c] Preparatively[3] 79% of *XII* were obtained. [d] Preparatively[3] 92% of *XXVIII* were obtained.

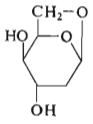
Dianhydro derivatives *I*–*IV* reacted with 5% potassium hydroxide in water at 100°C practically quantitatively in 5 to 6 hours, giving rise to vicinal diols *XIII* to *XVI*. Decomposition which we observed earlier[4] with epoxy derivatives of 1,6-anhydrohexopyranoses with *cis* arrangement of the epoxide ring and the hydroxyl group were not observed in any of our present cases. From dianhydride *I* a mixture of diols *XIV* and *XV* was formed, from dianhydride *II* the diol *XIV* was formed quantitatively, which corroborated our earlier results[1]. Under the same conditions dianhydride *III* gave a mixture of diols *XIII* and *XVI*, while dianhydride *IV* gave a single product, diol *XIII*. The products in the reaction mixture were analysed in the

form of their trimethylsilyl derivatives by gas chromatography, comparing them with authentic samples prepared on reduction of suitable 1,6:2,3- and 1,6:3,4-dinahydro-β-D-hexopyranoses on Raney nickel[7].

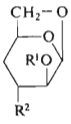
The reaction of dianhydro derivatives *I–IV* with magnesium iodide etherate was carried out in ether at room temperature, and it took 30–60 minutes under formation of vicinal iodohydrins. From dianhydride *I* iodohydrin *XVII* was formed, from dianhydride *II* iodohydrin *XXII*, while from dianhydride *III* a mixture of iodo-



XIV



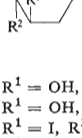
XVI



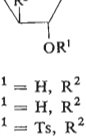
XV, $R^1 = H$, $R^2 = OH$
XVII, $R^1 = H$, $R^2 = I$
XVIII, $R^1 = H$, $R^2 = H$
XIX, $R^1 = Ts$, $R^2 = H$

Ts = p-$CH_3C_6H_4SO_2$—

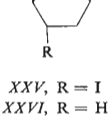
hydrins *XX* and *XXV*, and from dianhydride *IV* a single iodohydrin *XXVII* were formed. The structures of the iodohydrins were proved by reaction with sodium methoxide, during which starting dianhydro derivatives were formed, and also by catalytic deiodination on Raney nickel affording dideoxy derivatives of 1,6-anhydro-β-D-hexopyranoses which were compared with the hydrogenation products of dianhydro derivatives *I–IV*, or also with the products of their reduction with lithium aluminum hydride. Methylmagnesium iodide behaved similarly as magnesium iodide: as the main products, the mentioned iodohydrins were isolated, but according to thin-layer chromatography the reaction mixture also contained a small amount of by-products. Therefore, we studied further only the reaction with magnesium iodide which was more suitable for the preparation of iodohydrins.



XX, $R^1 = OH$, $R^2 = I$
XXI, $R^1 = OH$, $R^2 = H$
XXVII, $R^1 = I$, $R^2 = OH$
XXVIII, $R^1 = H$, $R^2 = OH$
XXIX, $R^1 = H$, $R^2 = OTs$



XXII, $R^1 = H$, $R^2 = I$
XXIII, $R^1 = H$, $R^2 = H$
XXIV, $R^1 = Ts$, $R^2 = H$



XXV, R = I
XXVI, R = H

Ts = p-$CH_3C_6H_4SO_2$—

Catalytic hydrogenation of dianhydro derivatives *I*–*IV* took place at 40°C in ethanolic solution in the presence of Raney nickel and it was usually completed after a few hours. Dianhydride *I* gave 1,6-anhydro-3,4-dideoxy-β-D-*threo*-hexopyranose (*XVIII*) and 1,6-anhydro-2,4-dideoxy-β-D-*threo*-hexopyranose (*XXI*), dianhydride *II* led to 1,6-anhydro-3,4-dideoxy-β-D-*erythro*-hexopyranose (*XXIII*), dianhydride *III* afforded 2,4-dideoxy derivative *XXI* and 1,6-anhydro-2,3-dideoxy-β-D-*threo*-hexopyranose (*XXVI*), and 1,6-anhydro-2,3-dideoxy-β-D-*erythro*-hexopyranose (*XXVIII*) was formed from dianhydride *IV*. In addition to the expected dideoxy derivatives of 1,6-anhydro-β-D-hexopyranoses we proved in all instances the formation of 1,6-anhydro-2,3,4-trideoxy-β-D-hexopyranose[2] (*XXXI*) in 4–9% yields.* The composition of the reaction mixtures was determined gas chromatographically and by thin-layer chromatography. The structure of dideoxy derivatives was determined by several independent methods. Thus the structure of substances *XVIII*, *XXI* and *XXVI* followed from the comparison of the reaction mixtures after the reduction of dianhydride *I* and *III* which contained dideoxy derivative *XXI* in both cases; from this the structure of substances *XVIII* and *XXVI* followed. It was further corroborated by oxidation of the dideoxy derivatives to 2-, 3- or 4-oxo-derivatives of trideoxy compound *XXXI* and by their reduction to corresponding alcohols[8]. The correctness of the structures proposed for dideoxy derivatives *XVIII*, *XXIII* and *XXVIII* was confirmed by optical rotation measurements (Table II). The mentioned substances were characterized as *p*-toluenesulfonyl derivatives *XIX*, *XXIV* and *XXIX*, of which the last was identical with the product prepared from 1,6-anhydro-4-O-benzyl-2,3-dideoxy-β-D-*erythro*-2-hexenopyranose on reduction, catalytic debenzylation, and tosylation[2].

TABLE II

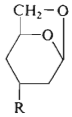
Optical Rotation of Dideoxy Derivatives of 1,6-Anhydrohexopyranoses

Substance	*XVIII*	*XXIII*	*XXVIII*
$[\alpha]_D$ found (H_2O)	−133°	−58°	−116° [b]
$[\alpha]_D$ calculated[a]	−137°	−60°	−126°

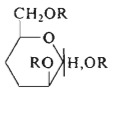
[a] $[\alpha]_D$ Values were calculated according to literature[2,6] using the parameters for the basic skeleton of 1,6-anhydro-β-D-hexopyranose (−79°) and for partial contributions of hydroxyl groups in the position 2 (±31°) and 4 (±22°), and they were corrected for m.w. 130. [b] Literature[2] gives $[\alpha]_D$ −119° (H_2O).

* Reductive splitting off of the oxiran ring oxygen was also observed during the reduction of 1,6:2,3- and 1,6:3,4-dianhydro-β-D-hexopyranoses, the yields[7] of dideoxy derivatives of 1,6-anhydro-β-D-hexopyranoses were about 14 to 20%.

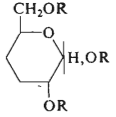
The reduction of dianhydro derivatives *I*–*IV* with lithium aluminum hydride was carried out in tetrahydrofuran at room temperature for 72 h. The reaction mixture was decomposed with water, filtered, evaporated to dryness, the residue extracted with ethanol and analysed as in the case of catalytic hydrogenation. The composition of the reaction mixture was similar as in the case of catalytic hydrogenation. From dianhydrides *II* and *IV* single products were formed, *i.e.* dideoxy derivatives *XXIII* and *XXVIII*, while from dianhydride *I* and *III* mixtures of dideoxy derivatives *XVIII*, *XXI*, and *XXI*, *XXVI*, resp., were obtained. The formation of trideoxy derivative *XXXI* was not observed.



XXX, R = OH
XXXI, R = H



XXXII, R = $COCH_3$
XXXIII, R = H



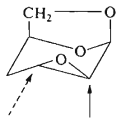
XXXIV, R = $COCH_3$
XXXV, R = H

Dideoxy derivatives *XVIII* and *XXIII*, which are well accessible in larger quantities by the above described procedures, were transformed on acetolysis to corresponding tri-O-acetyl derivatives of the reducing hexoses *XXXII* and *XXXIV*, the catalytic deacetylation of which with sodium methoxide gave free hexoses. From dideoxy derivative *XXIII* crystalline 3,4-dideoxy-D-*erythro*-hexopyranose (*XXXV*)* was obtained by this procedure (and also by direct hydrolysis with Amberlite IR 120); it was probably in its β-anomeric form, as indicated by the course of mutarotation. Although the dianhydro derivative *XVIII* afforded on acetolysis crystalline acetate of dideoxyhexose *XXXII*, its deacetylation gave a syrupy, analytically not quite pure, 3,4-dideoxy-D-*threo*-hexopyranose (*XXXIII*).

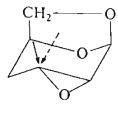
While alkaline hydrolysis of deoxy epoxides *II* and *IV* took place under formation of diaxial products – as also in the case of 1,6:2,3- and 1,6:3,4-dianhydro-β-D-hexopyranoses[4], deoxy epoxides *I* and *III* gave an appreciable amount of diequatorial products under the same conditions. As these systems are practically completely rigid, we consider the equatorial splitting as one of the proofs that polar effects[10] play an appreciable role in the opening of the epoxide rings: the epoxide substituted on the vicinal carbon atom with an electronegative group is first attacked on that epoxide carbon atom which is farthest from the electronegative substituent, in our case the oxygen atom (Scheme 1). If sterical and polar effects are synergistic, uniform (pure) products are formed, if they are antagonistic the result is an unselective reac-

* Methyl 3,4-dideoxy-α-D-*erythro*-hexopyranoside was recently described by Japanese authors[9].

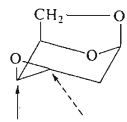
tion course. Quantitative data on the cleavage of epoxides *I* and *III*, when in the first case a larger amount of the diequatorial product is formed, are probably a consequence of the greater electronegativity of the $C\overset{O}{\diagdown\!\diagup O}$ group in comparison with the C—O group. Methyl 6-O-acetyl-2,3-anhydro-4-deoxy-α-DL-*ribo*-hexopyranoside gives with 5% potassium hydroxide a mixture of *xylo*- and *arabino*-glycoside in a 93 : 7 ratio, while the corresponding 4-deoxy-*lyxo* derivative affords only *arabino*-glycoside[11].



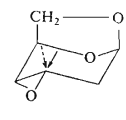
Ia



IIa



IIIa



IVa

↑ polar controlled reaction ↑ sterically controlled reaction

6-Deoxy derivatives of the mentioned compounds react in a similar manner with potassium hydroxide[12], ammonia[13], or dimethylamine[14] (*cf.* ref[15,16]). From this it may be concluded that in the case of systems with a flexible conformation the formation of the products of diequatorial splitting is more pronounced (if it corresponds to the polarity of the oxiran ring) than in other similar rigid systems. Reduction of dianhydrides *I*—*IV* with lithium aluminum hydride took place predominantly under formation of diaxial products, similarly as in the case of other bicyclic sugar epoxides[5,17] and 3-oxatricyclo[4.2.1.$0^{2,4}$]nonane[18]. In comparison with the hydroxyl ions (5% KOH) $LiAlH_4$ seems to be a reagent with greater sterical requirements and less sensitivity towards the molecule polarity. Reduction of dianhydrides *I*—*IV* with hydrogen on Raney nickel is from the point of view of the sterical course similar

TABLE III

Gas Chromatography of Dideoxy Derivatives of 1,6-Anhydro-β-D-hexopyranoses

Substance	*XXI*	*XXVIII*	*XXIII*	*XVIII*	*XXVI*	*XXX*
Rel. ret. time[a]	0·86[b]	0·97	1·00[c]	1·25	1·79[b]	1·88[b]

[a] Column No 2: $T = 166°C$ ($T_i = 200°C$), nitrogen flow 36 ml/min. [b] For the preparation of this compound see ref.[8]. [c] Retention time 8·3 min.

to the reaction with 5% potassium hydroxide, as if it were appreciably affected by the polarity of the molecule. Our interpretation of the results of catalytic reduction of 1,6:2,3- and 1,6:3,4-dianhydro-β-D-hexopyranoses[7] was based on the same consideration, and its correctness was confirmed during the reduction of deoxy anhydrides *I* and *III*, when the amount of 3-deoxy derivatives (Table I) in the reaction mixture increased according to our expectation.

Of all reagents discussed in this paper magnesium iodide in ether was most selective for the cleavage of the oxiran ring. While the reaction with *ribo*-derivatives *II* and *IV* took place exclusively diaxially – although complications could be expected, due to 1,3-interactions of the entering iodide anion with 1,6-anhydride bridge – 3-iodo derivative *XVII* was surprisingly formed from 4-deoxy-*lyxo* derivative *I* as the sole product. This means that a diequatorial attack of the oxiran ring took place exclusively. In contrast to this benzyl epoxide *V* gave on reaction with magnesium iodide practically exclusively 2-iodo derivative of *gluco*-configuration *VII*, *i.e.* a product of diaxial cleavage. From literature[19–21] it is known that methyl 2,3-anhydro--4,6-O-benzylidene-α-D-allopyranoside reacts with "aged" methylmagnesium iodide in tetrahydrofuran diequatorially under formation of 3-iodo derivative, while under other conditions it gives 2-iodo derivative[19,22,23]. However, it is possible that on reaction of epoxide *I* with magnesium iodide the attacking reagent is not the iodide ion itself, but that the magnesium cation also participates, possibly under formation of a complex.* Neither the conflicting literature data[19–23] nor our own results enable a satisfactory explanation.

This study confirmed that the reactions of sugar epoxides, especially those of deoxy sugars, should be explained by a synergy of steric and polar effects. 1,6-Anhydrohexopyranoses in their rigid C_4^1 conformation react under formation of products the quantitative composition of which is different from that obtained from the corresponding hexopyranosides in C_1^4 conformation.

EXPERIMENTAL

The melting points were determined on a Boëtius micromelting point apparatus. Optical rotations were measured with an automatic polarimeter Bendix Ericsson, UK Ltd, type 143 A, at 23–25°C. All reactions were followed by thin layer chromatography on silica gel according to Stahl (0·2–0·3 mm layer thickness) in benzene–acetone (9 : 1), detection with 50% sulfuric acid and heating; in the case of epoxy derivatives the detection with sodium iodide according to Buchanan[25] was also applied.

Gas chromatography was carried out on Chrom 3 (Laboratorní přístroje) in glass columns, using FID; quantitative analyses were performed by evaluating the areas of the peaks and com-

* In a similar manner as with magnesium iodide epoxide *I* also reacts with anhydrous hydriodic acid in a mixture of chloroform and dioxan under formation of iodohydrin *XVII* in about 90% yield. The reaction takes place faster and it is evidently started by protonation of the oxiran ring[24].

parison with the responses of standards. Column No 1 : 193 cm × 5 mm, Chromosorb W-AW HMDS (60—80 mesh) coated with 3·5% of OV-101 phase (Analabs). Column No 2 : 182 cm × × 5 mm, Chromosorb W-AW (80—100 mesh) impregnated with 15% of Carbowax 20 M. Column No 3 : 185 cm × 5 mm, Chromosorb W-AW (100—120 mesh) impregnated with 25% of Apiezon L. The solutions were concentrated on a rotary evaporator *in vacuo*, at as low a temperature as possible. During the working up of the reaction mixtures containing 2-deoxy derivatives of 1,6-anhydrohexoses the pH value was controlled and kept within the 5—8 interval because these substances are generally easily cleaved in acid medium. Samples for analysis, with the exception of distilled products, were dried under reduced pressure over phosphorus pentoxide. Magnesium iodide was prepared by refluxing 2·85 g of magnesium (for Grignard reaction) with 29·5 g of iodine in 300 ml of ether for about 6 hours, under exclusion of moisture, until the reaction mixture was decolorized. The ethereal layer was then cooled and decanted from the remains of magnesium and sedimented impurities. On standing diethyl etherate of magnesium iodide crystallised out.

1,6-Anhydro-4-O-benzyl-2-deoxy-2-iodo-β-D-glucopyranose (*VII*)

An emulsion of melted magnesium iodide etherate (20 g); in a small amount of ether was added dropwise to a solution of 10 g of benzyl epoxide[4] *V* in 250 ml of ether and the mixture was shaken at room temperature. The course of the reaction was followed chromatographically on thin layer; after 30 minutes shaking the starting epoxide disappeared. The mixture was poured into an equal amount of ice-cooled 1% hydrochloric acid and neutralised with solid sodium hydrogen carbonate to pH 5—6. The ethereal layer was separated and the aqueous extracted with five 100 ml portions of chloroform. The combined extracts were dried over anhydrous magnesium sulfate and allowed to stand over active charcoal. After filtration the solvents were distilled off and the remaining syrup dissolved in a minimum amount of ether and diluted with light petroleum. After standing in a refrigerator 14·3 g (92%) of a substance were obtained which melted at 83°C, $[\alpha]_D$ +42° (*c* 1·3; chloroform). For analysis the product was recrystallised from an ether–light petroleum mixture. For $C_{13}H_{15}IO_4$ (362·2) calculated: 43·11% C, 4·17% H, 35·03% I; found: 43·50% C, 4·36% H, 34·91% I.

1,6-Anhydro-4-O-benzyl-2-deoxy-β-D-*arabino*-hexopyranose (*VI*)

To a solution of 20 g of 2-iodo derivative *VII* in 200 ml of ethanol 40 g of sodium hydrogen carbonate and 50 ml of a suspension of Raney nickel[6] in ethanol were added and the reaction mixture shaken under hydrogen and heating with an infrared lamp at about 40°C. After two hours dehalogenation was ended, the catalyst filtered off and washed with 25 ml of hot ethanol and 50 ml of hot acetone. The combined extracts were distilled off and the residue dissolved in 300 ml of water. The aqueous solution was extracted five times with 200 ml portions of chloroform, the extracts were combined and dried over anhydrous magnesium sulfate and filtered with active charcoal. After evaporation of the solvent 12 g (92%) of a residue were obtained which was treated with ether and light petroleum and allowed to stand in a refrigerator to crystallise. After several days standing crystals were obtained which were recrystallised from an ether–light petroleum mixture; m.p. 38—41°C, $[\alpha]_D$ −51° (*c* 0·4; chloroform). For $C_{13}H_{16}O_4$ (236·3) calculated: 66·07% C, 6·82% H; found: 66·11% C, 6·84% H.

1,6-Anhydro-4-O-benzyl-2-deoxy-3-O-*p*-toluenesulfonyl-β-D-*arabino*-hexopyranose (*VIII*)

p-Toluenesulfonyl chloride (15 g) was added in several portions to a solution of 6·2 g of benzyl derivative *VI* in 50 ml of pyridine and the reaction mixture allowed to stand at room temperatrure

for 24 h. It was then poured into 500 m of water with ice, 20 ml of ether were added and the mixture stirred until a crystalline product separated out. Its recrystallisation from ethanol gave 8·3 g (82%) of crystals of m.p. 125—126°C, $[\alpha]_D$ +23° (*c* 0·77; chloroform). For $C_{20}H_{22}O_6S$ (390·4) calculated: 61·52% C, 5·62% H, 8·21% S; found: 61·36% C, 5·71% H, 7·93% S.

1,6-Anhydro-2-deoxy-3-O-*p*-toluenesulfonyl-β-D-*arabino*-hexopyranose (*IX*)

Benzyltosylate *VIII* (15 g) in 200 ml of redistilled acetic acid was additioned with 3 g of 10% palladium on charcoal and hydrogenated at 40°C heating with infrared lamp for 8 h. The mixture was filtered, the filtrate diluted with 500 ml of water, neutralised with solid sodium hydrogen carbonate and extracted with three 100 ml portions of chloroform. The combined extracts were dried over anhydrous magnesium sulfate, filtered through a small column of active charcoal and evaporated to dryness. The residue was crystallised from a chloroform–ether–light petroleum mixture. Yield 8·5 g (71%), m.p. 86—87°C, $[\alpha]_D$ −51° (*c* 0·6; chloroform). For $C_{13}H_{16}O_6S$ (300·3) calculated: 51·99% C, 5·37% H, 10·68% S; found: 51·71% C, 5·35% H, 10·55% S.

1,6:3,4-Dianhydro-2-deoxy-β-D-*ribo*-hexopyranose (*IV*)

To a solution of 8·0 g of tosyl ester *IX* in 100 ml of chloroform a solution of 1·5 g of sodium in 30 ml of methanol was added dropwise under stirring and cooling with ice. After one hour standing chloroform was distilled off and the residue dissolved in 100 ml of water and extracted four times with 50 ml portions of chloroform. The chloroform solution was washed with a small amount of 1% hydrochloric acid and water, dried over anhydrous magnesium sulfate and decolorized with charcoal. After filtration chloroform was distilled off and the residue distilled in a Hickmann flask at 80°C bath temperature and 0·1 Torr. Yield 2·70 g (79%), $[\alpha]_D$ — 136° (*c* 0·75; water). For $C_6H_8O_3$ (128·1) calculated: 56·24% C, 6·29% H; found: 56·19% C, 6·15% H. Gas chromatography: column No 2, $T = 171$°C ($T_i = 205$°C), nitrogen flow rate 36 ml/min; relative retention time 0·97, rel. ret. times of dianhydrides *I*, *II* and *III* are 1·00 (ret. time 9·4 min), 1·12 and 0·70 resp.

3-O-Acetyl-1,6-anhydro-4-O-benzyl-2-deoxy-β-D-*arabino*-hexopyranose (*X*)

A mixture of 9·0 g of benzyl derivative *VI*, 20 ml of acetic anhydride and 15 g of anhydrous sodium acetate was heated on a boiling water bath for 5 min. After cooling the mixture was poured into 200 ml of icy water and the solution was neutralized with solid sodium hydrogen carbonate and extracted with three 300 ml portions of chloroform. The extract was dried over anhydrous magnesium sulfate and filtered with charcoal. After evaporation of the solvent 9·4 g (88%) of a syrup were obtained containing according to thin-layer chromatography only a small amount of impurities. For $C_{15}H_{18}O_5$ (278·3) calculated: 64·73% C, 6·74% H; found: 64·91% C, 6·64% H. The crude product was further worked up to tosylacetate *XII*.

3-O-Acetyl-1,6-anhydro-2-deoxy-4-O-*p*-toluenesulfonyl-β-D-*arabino*-hexopyranose (*XII*)

A solution of 5·0 g of benzyl derivative *X* in 30 ml of acetic acid was hydrogenated over 1 g of 10% palladium on charcoal at 40°C (infrared lamp). After 12 h when the reaction was practically over the catalyst was filtered off and the filtrate concentrated. The residue was dissolved in 50 ml of water and filtered with charcoal, and the filtrate extracted several times with chloroform. The combined chloroform extracts were dried over anhydrous magnesium sulfate, filtered with charcoal and chloroform distilled off. Yield 1·6 g (55%) of non-crystalline acetyl derivative *XI*.

To a solution of 4·8 g of acetyl derivative *XI* in pyridine 8·0 g of *p*-toluenesulfonyl chloride were added in several portions. The mixture was allowed to stand at room temperature for 48 h, then poured into 200 ml of water-and-ice mixture and additioned with 20 ml of ether. The mixture was stirred until a crystalline product separated out. After filtering it off the product was crystallised from ethanol. Yield 6·73 g (78%), m.p. 106–108°C, $[\alpha]_D$ −104° (*c* 0·8; chloroform). For $C_{15}H_{18}O_7S$ (342·4) calculated: 52·61% C, 5·29% H, 9·36% S; found: 52·72% C, 5·34% H, 9·46% S.

1,6:3,4-Dianhydro-2-deoxy-β-D-*lyxo*-hexopyranose (*III*)

To a solution of 1,5 g of tosyl derivative *XII* in 50 ml of chloroform 10 ml of a methanol solution containing 0·35 g of dissolved sodium were added under stirring and the reaction mixture allowed to stand at room temperature for 6 h. It was then poured into 100 ml of water and extracted with three 50 ml portions of chloroform. The organic layer was washed with 1% hydrochloric acid and water and then dried over anhydrous calcium chloride. After filtration with charcoal chloroform was evaporated and the remaining oil was distilled in a Hickmann flask at 80°C bath temperature and 0·1 Torr. Yield 0·45 g (80%) of viscous liquid, $[\alpha]_D$ −105° (*c* 0·6; water). For $C_6H_8O_3$ (128·1) calculated: 56·24% C, 6·29% H; found: 56·07% C, 6·32% H. Gas chromatography: column No 2, T = 171°C (T_i = 205°C), nitrogen flow 36 ml/min; relative retention time 0·70, relative retention times of dianhydrides *I*, *II* and *IV* are 1·00 (ret. time 9·4 min), 1·12 and 0·97 resp.

1,6-Anhydro-3,4-dideoxy-3-iodo-β-D-*arabino*-hexopyranose (*XVII*)

a) To a solution of 3·0 g of deoxyanhydride[1] *I* in 50 ml of ether 10 g of an emulsion of melted diethyl etherate of magnesium iodide in a few ml of ether was added and the mixture stirred at room temperature. When the reaction ceased (after 30–60 min) the mixture was poured into 500 ml of an ice-cool 1% hydrochloric acid solution and the pH value was adjusted with solid sodium hydrogen carbonate to 5–6. The ethereal layer was separated and the aqueous solution extracted five times with 100 ml chloroform portions. The combined extracts were dried over anhydrous magnesium sulfate, additioned with a small amount of sodium thiosulfate for binding free iodine, and filtered with charcoal. The filtrate was evaporated and the solid residue crystallised from an ether–light petroleum mixture (standing in refrigerator). On further crystallisation iodohydrin *XVII* was obtained in 78% yield (4·70 g), m.p. 115–117°C (subl.), $[\alpha]_D$ −145° (*c* 0·5; chloroform). For $C_6H_9IO_3$ (256·1) calculated: 28·14% C, 3·54% H, 49·59% I; found: 27·97% C, 3·52% H, 49·11% I.

b) To a solution of 3 g of deoxyanhydride[1] *I* in 50 ml of ether 20 g of methylmagnesium iodide in 300 ml of ether were added dropwise under stirring. The stirring was continued for another hour at room temperature (the end of the reaction was controlled by thin-layer chromatography) and the reaction mixture was poured into 500 ml of a 1% hydrochloric acid solution and neutralised under stirring with solid hydrogen carbonate (pH 5–6). The ethereal layer was separated and the aqueous layer was extracted with five 100 ml portions of chloroform. The combined organic extracts were dried over anhydrous magnesium sulfate and filtered with charcoal. The solution was concentrated and the solid residue crystallised from ether–light petroleum; the yield of *XVII* was 4·30 g (71%). The product had identical properties with iodohydrin *XVII* prepared as under *a*).

1,6-Anhydro-3,4-dideoxy-3-iodo-β-D-*xylo*-hexopyranose (*XXII*)

a) It was prepared on reaction of 2 g of deoxyanhydride[2] *II* with 3 g of magnesium iodide in ether by a procedure similar to that used in the preparation of iodohydrin *XVII*. Yield 1·5 g (75%), m.p. 64—66°C, $[\alpha]_D$ —5° (*c* 1·3; chloroform). For $C_6H_9IO_3$ (256·1) calculated: 28·14% C, 3·54% H, 49·59% I; found: 28·35% C, 3·50% H, 49·60% I.

b) An identical product was obtained on reaction of 1 g deoxyanhydride *II* with 7 g of methylmagnesium iodide applying a procedure similar as in the preparation of iodohydrin *XVII*.

1,6-Anhydro-2,4-dideoxy-4-iodo-β-D-*arabino*-hexopyranose (*XX*)
and 1,6-Anhydro-2,3-dideoxy-3-iodo-β-D-*xylo*-hexopyranose (*XXV*)

On reacting 1 g of deoxyanhydride *III* with 3 g of magnesium iodide according to procedure *a*) (as in the preparation of iodohydrin *XVII*) 1,2 g (60%) of a mixture of iodohydrins *XX* and *XXV* were obtained in which *XX* was the major component (after catalytic dehalogenation the ratio of the corresponding deoxy derivatives was determined to be 9 : 1, see Table I). The mixture was separated chromatographically on a column of 50 g of silica gel in a mixture of benzene and acetone (95 : 5). Iodohydrin *XX* was eluted from the column first and it was crystallised from ether–light petroleum mixture; m.p. 108—109°C, $[\alpha]_D$ —165° (*c* 0·3; chloroform). For $C_6H_9IO_3$ (256·1) calculated: 28·14% C, 3·54% H, 49·59% I; found: 28·37% C, 3·57% H, 49·11% I. The second iodohydrin *XXV* was not obtained in pure state.

1,6-Anhydro-2,3-dideoxy-3-iodo-β-D-*arabino*-hexopyranose (*XXVII*)

Reaction of 1 g of deoxyepoxide *IV* with 3 g of magnesium iodide etherate in 30 ml of ether (see the preparation of iodohydrin *XVII*, procedure *a*) gave iodohydrin *XXVII* in a 60% yield (1·2 g), m.p. 74—76°C, $[\alpha]_D$ —150° (*c* 0·5; chloroform). For $C_6H_9IO_3$ (256·1) calculated: 28·14% C, 3·54% H, 49·59% I; found: 28·40% C, 3·54% H, 49·26% I.

1,6-Anhydro-3,4-dideoxy-β-D-*threo*-hexopyranose (*XVIII*)

a) To a solution of 15 g of iodohydrin *XVII* in 100 ml of ethanol 15 ml of a Raney-nickel suspension[6] in ethanol and 20 g of barium carbonate were added and the mixture hydrogenated at 40—50°C (infrared lamp) for 6 h. When the dehalogenation was over the mixture was filtered and the residue on the filter was washed with warm acetone and the combined solutions were concentrated to a syrupy consistence. The syrup was dissolved in 100 ml of water and the solution filtered with charcoal and extracted continually with ether. The extract was dried over anhydrous magnesium sulfate, ether was distilled off and the remaining oil was distilled in a Hickmann flask at 0·5 Torr, bath temperature 120—140°C; yield 5·45 g (72%). After redistillation the product crystallised out, m.p. about 28°C (unsharp), $[\alpha]_D$ —133° (*c* 0·6; water). For $C_6H_{10}O_3$ (130·1) calculated: 55·41% C, 7·75% H; found: 55·58% C, 7·68% H.

b) Dideoxy derivative *XVIII* is also formed as the main product on reduction of dianhydride *I* on Raney nickel, and it is accompanied by dideoxy derivative *XXI* and trideoxy derivative *XXXI* (Table I.).

1,6-Anhydro-3,4-dideoxy-β-D-*erythro*-hexopyranose (*XXIII*)

a) On dehalogenation of 1·5 g of iodohydrin *XXII* in 20 ml of ethanol, in the presence of 3 ml of a Raney nickel[6] suspension and 2 g barium carbonate (see procedure *a*) in the preparation

of dideoxy derivative *XVIII*), 0·6 g (79%) of dideoxy derivative were obtained which was crystallised from a mixture of ether and light petroleum; m.p. 85—86°C, $[\alpha]_D$ —58° (*c* 0·7; water). For $C_6H_{10}O_3$ (130·1) calculated: 55·41% C, 7·75% H; found: 55·58% C, 7·68% H.

b) A solution of 0·5 g of dianhydro derivative *II* in 20 ml of ethanol was hydrogenated in the presence of 3 ml of a Raney nickel suspension[6] in ethanol at 40—50°C (infrared lamp). After 2 h the catalyst was filtered off, washed with hot ethanol and the combined ethanolic solutions were evaporated. The solid residue was crystallised from an ether–light-petroleum mixture. The yield of dideoxy derivative *XXIII* was 0·45 g (89%) and it was identical according to all its properties with the product prepared under *a*).

1,6-Anhydro-2,3-dideoxy-β-D-*erythro*-hexopyranose (*XXVIII*)

a) Catalytic dehalogenation of 0·3 g of iodohydrin *XXVII* (see procedure *a*) in the preparation of dideoxy derivative *XVIII*) gave 0·10 g (66%) of dideoxy derivative of m.p. 65—70°C, $[\alpha]_D$ —116° (*c* 0·3; chloroform). For $C_6H_{10}O_3$ (130·1) calculated: 55·41% C, 7·75% H; found: 55·28% C, 7·57% H. Literature[2] gives m.p. 65—70°C, $[\alpha]_D$ —119° (*c* 0·79; chloroform). Lit.[3] gives, for the racemate, m.p. 79—81°C.

b) A solution of 1 g of anhydro derivative *IV* in 30 ml of ethanol was hydrogenated with 10 ml of a Raney nickel suspension[6] in ethanol at 40—50°C for 4 h. After the catalyst had been filtered off and the solvent evaporated the residue was crystallised from an ether–light petroleum mixture. Yield 0·6 g (60%). The product was identical with the dideoxy derivative prepared by procedure *a*).

1,6-Anhydro-3,4-dideoxy-2-O-*p*-toluenesulfonyl-β-D-*threo*-hexopyranose (*XIX*)

To a solution of 0·15 g of dideoxy derivative *XVIII* in 2 ml of pyridine 0·3 g of *p*-toluenesulfonyl chloride was added and the mixture allowed to stand at room temperature for 24 h. It was then poured into 20 ml of water and extracted twice with 5 ml of chloroform. The extract was washed with water, dilute hydrochloric acid and again water, then dried over anhydrous magnesium sulfate and filtered with charcoal. After distillation off of the chloroform the residue was crystallised from a mixture of acetone, ether, and light petroleum. Yield 0·28 g (85%), m.p. 83—85°C $[\alpha]_D$ —82° (*c* 0·66; chloroform). For $C_{13}H_{16}O_5S$ (284·3) calculated: 54·91% C, 5·67% H, 11·28% S; found: 54·98% C, 5·65% H, 11·44% S.

1,6-Anhydro-3,4-dideoxy-2-O-*p*-toluenesulfonyl-β-D-*erythro*-hexopyranose (*XXIV*)

Tosylation of 0·2 g of dideoxy derivative *XXIII* in 2 ml of pyridine with 0·4 g of *p*-toluenesulfonyl chloride using the same procedure as in the preparation of ester *XIX* gave 0·4 g (91%) of substance of m.p. 84—86°C, $[\alpha]_D$ —42° (*c* 0·8; chloroform). For $C_{13}H_{16}O_5S$ (284·3) calculated: 54·91% C, 5·67% H, 11·28% S; found: 55·06% C, 5·87% H, 11·34% S.

1,2,6-Tri-O-acetyl-3,4-dideoxy-α-D-*threo*-hexopyranose (*XXXII*)

To a solution of 0·5 g of dideoxy derivative *XVIII* in 2 ml of acetic anhydride a solution of 0·2 ml of 70% perchloric acid in 10 ml of acetic anhydride was added dropwise under cooling and stirring and the mixture after standing overnight was poured into 50 ml of water and ice mixture. The solution was extracted with three 50 ml portions of chloroform, the extract dried over anhydrous magnesium sulfate and shaken with charcoal. After filtration and evaporation of chloro-

form 0·9 g of an oil were obtained which was redissolved in chloroform and filtered through a small column of alumina and charcoal. After evaporation of the oily solution the residue weighed 0·75 g (71%). It was dissolved in a small amount of ether and diluted with light petroleum until turbidity appeared. It was then allowed to stand in a refrigerator. (The solution contained two products, probably both anomeric acetates. Gas chromatography: column 260 cm × 5 mm; chromosorb W-AW with 3% SE-30, $T = 162°C$, $T_i = 195°C$, nitrogen flow 36 ml/min). A product (0·4 g; 39%) crystallised out which after recrystallisation from ether–light petroleum mixture had m.p. 97—100°C, $[\alpha]_D$ +97° (*c* 0·6; chloroform). For $C_{12}H_{18}O_7$ (274·2) calculated: 52·51% C, 6·56% H; found: 52·32% C, 6·64% H.

3,4-Dideoxy-D-*threo*-hexose (*XXXIII*)

To a solution of 0·3 g of triacetyl derivative *XXXII* in 10 ml of ethanol a methanolic sodium solution (10 mg in 1 ml) was added and allowed to stand for 30 min at room temperature. Dowex 50 (1 g) was then added, and the solution filtered through a layer of silica gel and charcoal and concentrated. Yield 0·15 g (98%). The product reduces a Fehling's solution. Paper chromatography: Whatman No 3, 1-butanol–water, R_F 0·43, R_{DR} (relative to 2-deoxyribose) 1·53. Detection with ammoniacal $AgNO_3$.

1,2,6-Tri-O-acetyl-3,4-dideoxy-α,β-D-*erythro*-hexopyranose (*XXXIV*)

0·5 g of dideoxy derivative *XXIII* were acetolysed as in the preparation of triacetate *XXXII*. A syrup (0·75 g; 71%) was obtained which contained two substances, probably the two possible anomers. (Gas chromatography: column 260 cm × 5 mm; Chromosorb W-AW with 3% SE-30, $T = 177°C$, $T_i = 210°C$, nitrogen flow 16 ml/min. The crude product was deacetylated to dideoxyhexose *XXXV*.

3,4-Dideoxy-β-D-*erythro*-hexose (*XXXV*)

a) Deacetylation of 0·3 g of triacetate *XXXIV* was carried out as in the case of deacetylation of triacetate *XXXII*. After working up a syrup was obtained (0·15 g; 98%) which crystallised on standing in a desiccator. The product was recrystallised from methanol–ether. The crystals reduced Fehling's solution and melted at 101—103°C, $[\alpha]_D$ −10° (after 3 min) +10° (72 min, const.) (*c* 0·7; water). Paper chromatography: Whatman No 3, 1-butanol–water, R_F 0·39, R_{DR} (relative to 2-deoxyribose) 1·39, detection with ammoniacal silver nitrate. For $C_6H_{12}O_4$ (148·2) calculated: 48·63% C, 8·16% H; found: 48·94% C, 8·19% H.

b) A solution of 0·5 g of dideoxy derivative *XXIII* in 50 ml of water was refluxed under stirring with 1 g of Amberlite IR 120 in H^+ form for 6 h. The aqueous solution was filtered through a small layer of active charcoal under addition of a small amount of barium carbonate. Evaporation of the solution gave 0·4 g (70%) of a syrup containing a small amount of the starting compound. The product was isolated by preparative paper chromatography on Whatman paper No 3 and crystallised from a mixture of methanol and ether. The crystalline hexose was identical with the deacetylation product obtained under *a*).

Reaction of Dianhydro Derivatives *I*—*IV*, Quantitative Analysis

a) *With 5% potassium hydroxide* (see data in Table I): A solution of 10 mg of dianhydro derivative *I*—*IV* in 200 µl of a 5% potassium hydroxide solution was heated in a sealed tube on a boiling

water bath for 5 h. The reaction mixture was poured on a column of Dowex 50 W in H^+ form and the diols were eluted with water. The aqueous solution was concentrated under reduced pressure and the residue dissolved in 1 ml of pyridine. Hexamethyldisilazane (200 µl) and trimethylchlorosilane (100 µl) was added to the solution which was shaken and allowed to stand for 5 min. The solutions were then transferred onto chromatographic column No 1 (see the introductory section of Experimental) and chromatographed at 136°C (nitrogen flow 35 ml/min; see data in Table I).

b) *Catalytic hydrogenation* (see data in Table I and Table III): A solution of 25 mg of dianhydro derivative *I—IV* in 2 ml of ethanol was hydrogenated in the presence of approx. 0·1 ml of Raney nickel T-1[6] at 40°C and normal pressure for 15 h. After this the reaction mixture did not contain the starting material in any case. The samples were taken directly from the reaction mixture and were analysed on a column No 2.

c) *Reduction with lithium aluminum hydride* (see data in Table I): To a solution of 5 mg of dianhydride *I—IV* in 0·2 ml of tetrahydrofuran (distilled over lithium aluminum hydride) a solution of lithium aluminum hydride (2·5 mg) in 50 µl tetrahydrofuran was added dropwise and the mixture allowed to stand at room temperature for 3 days. A few drops of water were then added under cooling and after decomposition of the hydride the mixture was evaporated under reduced pressure to dryness. The residue was extracted with a small amount of hot ethanol. The ethanolic solution of dideoxy derivatives was injected into the column No 2 and 3 used for the analysis of the products of catalytic hydrogenation of dianhydrides.

d) *Reaction with magnesium iodide, reductive dehalogenation of iodohydrins* (see data in Table I): Dianhydro derivatives *I—IV* were transformed on reaction with magnesium iodide to iodohydrins under the same conditions as in the preparation of iodohydrin *XVII*. The crude mixture of iodohydrins was catalytically dehalogenated (see the preparation of dideoxy derivative *XVIII*) and the obtained mixtures of dideoxy derivatives in ethanol were analysed gas chromatographically under the same conditions as in the measurement of the reduction of dianhydro derivatives.

e) *Reaction of iodohydrins with sodium methoxide*: To a solution of 1·5 mg of sodium in 0·2 ml of methanol 5 mg of iodohydrin were added and the reaction mixture allowed to stand at room temperature for 1 h. The reaction mixture was introduced into a column and the dianhydro derivatives *I—IV* were identified by comparison with authentic samples. Chromatographic column No 2 was employed; *T* 171°C, nitrogen flow rate 36 ml/min.

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REFERENCES

1. Černý M., Pacák J.: This Journal *27*, 94 (1962).
2. Pecka J., Černý M.: This Journal *38*, 132 (1973).
3. Murray T. P., Singh U. P., Brown R. K.: Can. J. Chem. *49*, 2132 (1971).
4. Trnka T., Černý M.: This Journal *36*, 2216 (1971).
5. Seib P. A.: J. Chem. Soc. *1969*, 2552.
6. Dominguez X. A., Lopez I. C., Franco R.: J. Org. Chem. *26*, 1625 (1961).
7. Trnka T., Černý M.: This Journal *37*, 3632 (1972).
8. Pecka J., Staněk J. jr, Černý M.: This Journal, in press.
9. Umezawa S., Tsuchiya T., Okazaki Y.: Bull. Chem. Soc. Japan *44*, 2494 (1971).

10. Parker R. E., Isaacs N. S.: Chem. Rev. *58*, 737 (1959).
11. Konowal A., Zamojski A.: Roczniki Chem. *45*, 859 (1971).
12. Banaszek A., Zamojski A.: Roczniki Chem. *45*, 391 (1971).
13. Kefurt K., Čapek K., Čapková J., Kefurtová Z., Jarý J.: This Journal *37*, 2985 (1972).
14. Newman H.: J. Org. Chem. *29*, 1461 (1964).
15. Močalin V. B., Poršnev J. N., Samochvalov G. I., Janotovskij M. C.: Ž. Obšč. Chim. *39*, 116 (1969).
16. Močalin V. B., Poršnev J. N., Samochvalov G. I.: Ž. Obšč. Chim. *39*, 701 (1969).
17. Prins D. A.: J. Am. Chem. Soc. *70*, 3955 (1948).
18. Sauers R. R., How H. M., Feilich H.: Tetrahedron *21*, 983 (1965).
19. Inch T. D., Lewis G. J.: Carbohydrate Res. *15*, 1 (1970).
20. Richards G. N., Wiggins L. F.: J. Chem. Soc. *1953*, 2442.
21. Newth F. H., Richards G. N., Wiggins L. F.: J. Chem. Soc. *1950*, 2356.
22. Lemieux R. U., Fraga E., Watanabe K. A.: Can. J. Chem. *46*, 61 (1968).
23. Sharma M., Brown R. K.: Can. J. Chem. *46*, 757 (1968).
24. Trnka T., Černý M.: Unpublished results.
25. Buchanan J. G., Schwarz J. C. P.: J. Chem. Soc. *1962*, 4770.
26. Černý M., Pacák J., Staněk J.: Chem. Ind. (London) *1966*, 1559.

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