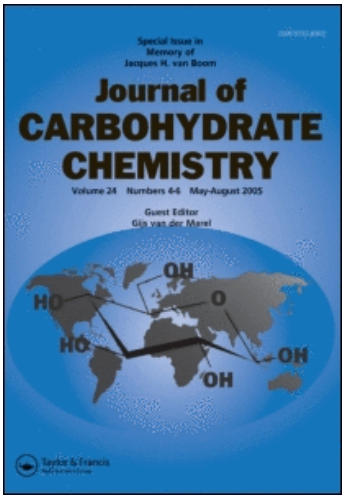

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SYNTHESIS OF HIGHER CARBON SUGARS VIA COUPLING OF SIMPLE MONOSACCHARIDES-WITTIG, HORNER-EMMONS, AND RELATED METHODS

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REVIEW

SYNTHESIS OF HIGHER CARBON SUGARS VIA COUPLING OF SIMPLE MONOSACCHARIDES–WITTIG, HORNER–EMMONS, AND RELATED METHODS

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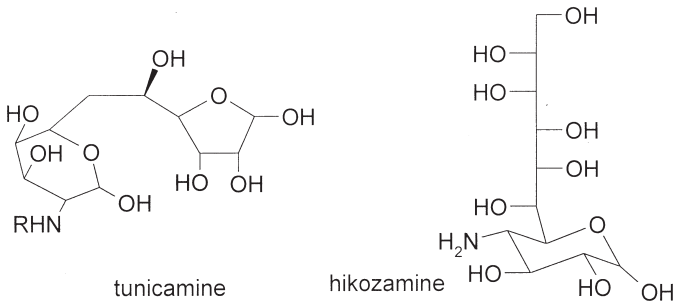
Dedicated to Professor Joachim Thiem on the occasion of his 60th birthday.

TABLE OF CONTENTS

1. INTRODUCTION

Higher carbon sugars (in particular those containing more than ten carbon atoms in the chain) have attracted wide attention in the last two decades as important (although not very common) components of some antibiotics, *e.g.*, tunicamine, a backbone of tunicamycin.[1] Until the end of the 1970s only very limited examples



of the synthesis or isolation of such higher carbon sugars were reported in the literature. The first example of a C-C-linked disaccharide, a dodecitol (by-product of electroreduction of D-glucose), was described in 1951 by Wolfrom.[2] In 1969, Ferrier and Prasad[3] reported a "dimer" obtained from 3,4,6-tri-*O*-acetyl-D-glucal, and in 1971 Roy and Chilton[4] synthesized a diastereoisomeric mixture of hexadecitols from 2,3:5,6-di-*O*-isopropylidene-D-mannose and acetylene. Paulsen and coworkers[5] introduced the methodology of coupling sugar derived dithiane anions with sugar aldehydes in 1976. The Secrist and Barnes directed synthesis[6] of a specific higher carbon sugar – hikozamine – was reported in 1979; a year later tunicamine was prepared by Suami and coworkers.[7]

Over the past twenty years the number of papers devoted to the synthesis of higher carbon sugars has rapidly increased. Many different methodologies, utilizing sugar acetylenes, carbohydrate-derived Wittig reagents, nitro-, diazo-sugars, aldol type condensations and glycosyl anions were applied. Recent reports on the syntheses of higher carbon sugars are found in reference 8.

2. SYNTHESIS OF HIGHER CARBON DIALDOSE PRECURSORS

Our synthetic plan for the preparation of higher carbon sugars is outlined in Fig. 1. The first step consists in coupling of two suitably activated monosaccharide sub-units either directly (n = 0), or *via* additional *C*-atom(s). The precursor thus obtained has a skeleton with the required number of the carbon atoms in the chain and can be further converted into a higher monosaccharide.

We elaborated several approaches leading to a higher sugar skeleton, based on the coupling of sugar-derived Wittig-type reagents (phosphoranes and phos-

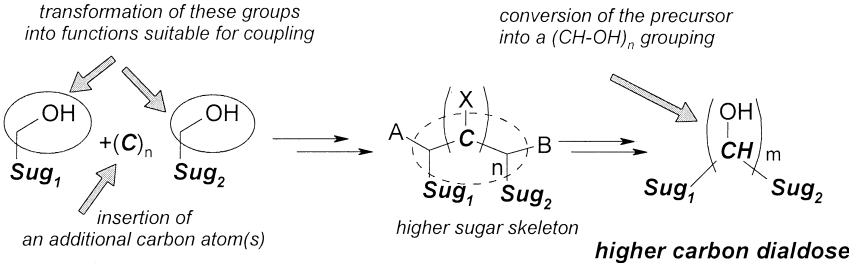


Figure 1. A strategy for the synthesis of higher carbon dialdoses.

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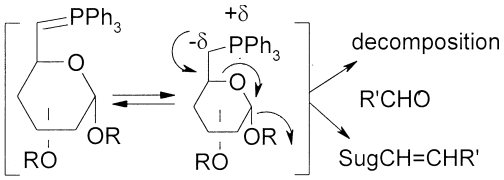


Figure 2.

phonates), sugar acetylenes (and vinyltin derivatives), and sugar allyltins with monosaccharide aldehydes.

All these methods will be described separately. The emphasis will be put on the Wittig-type and alkyne/vinyltin methodologies, which at present have the widest application in the synthesis of higher carbon sugars in our laboratory.

Finally, transformation of such precursors into higher sugars will be presented which should outline the usefulness of the method.

2.1. Higher Carbon Dialdose Precursors by a Wittig-Type Methodology

In their approach to the synthesis of hikozamine, Secrist and Barnes employed a Wittig methodology for coupling of two sugar sub-units. An unstabilized, sugar-derived phosphorane reacted with an aldehyde to provide an olefinic precursor (SugCH=CHR).[6] However, partial negative charge on the ylid C-atom induced a decomposition of the ylid and great care had be taken to obtain the desired higher sugar precursor (Fig. 2). To overcome such difficulties we decided to use stabilized sugar-derived phosphoranes in which this type of β-elimination is not possible.

The first step in our Wittig methodology consisted in conversion of a monosaccharide into a uronic acid. Reaction of the acid with *N,N′*-carbonyl diimidazole afforded a very reactive (and usually unstable) imidazolide, which upon treatment with $Ph_3P{=}CH_2$ (at least 2 equiv), was converted into a stabilized phosphorane. In the next step this ylid reacted with a sugar aldehyde to afford the corresponding enone (Fig. 3).

Our first paper utilizing the Wittig methodology to higher carbon sugars appeared in 1986.[9] Starting from 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranuronic acid, the corresponding phosphorane **1** was obtained in 73% yield. Similarly over the next few years we prepared other useful precursors such as: **2**,[10] **3**,[11] and **4**.[12] Compounds **1–3** reacted readily with sugar aldehydes to afford the corre-

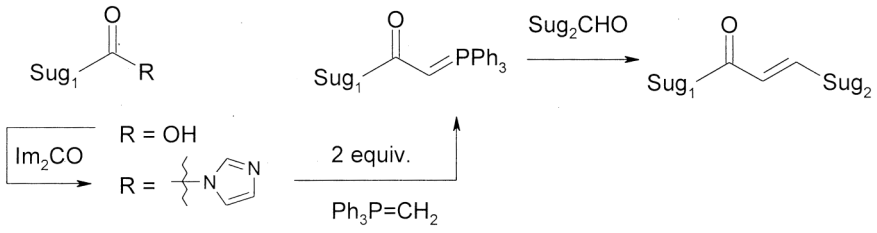
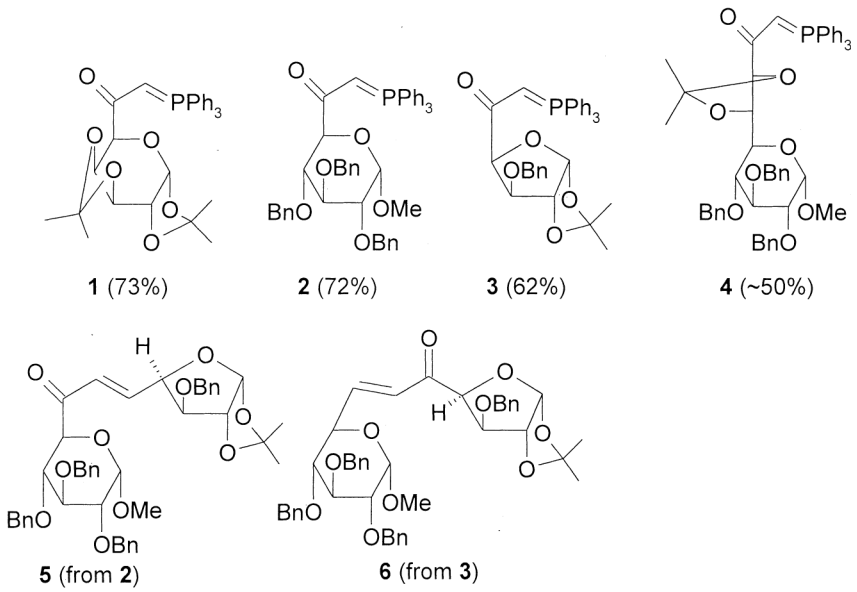


Figure 3. Synthesis of higher sugar skeleton by a Wittig methodology.



sponding enones (*e.g.* **5** or regioisomeric compound **6**) in good yields.[10,11] This reaction proceeds usually at room or slightly elevated temperature in solvents such as benzene or toluene. However, ylid **4** was extremely unreactive for reasons yet unknown and did not react even with simplest aldehydes (CH_3CHO, 2,3-*O*-isopropylidene-D-glyceraldehyde *etc.*) under standard conditions.[12]

This inertness was overcome when the Wittig reaction was performed under high pressure. Alternatively, reactivity could be improved by utilizing phosphonates in place of phosphoranes (i.e. Horner–Emmons procedure).

The sugar-derived phosphonates are easily prepared by reaction of the corresponding uronates with dimethyl methyl phosphonate anion.[12,13] The important feature of this methodology is, that the phosphonates can be obtained in much

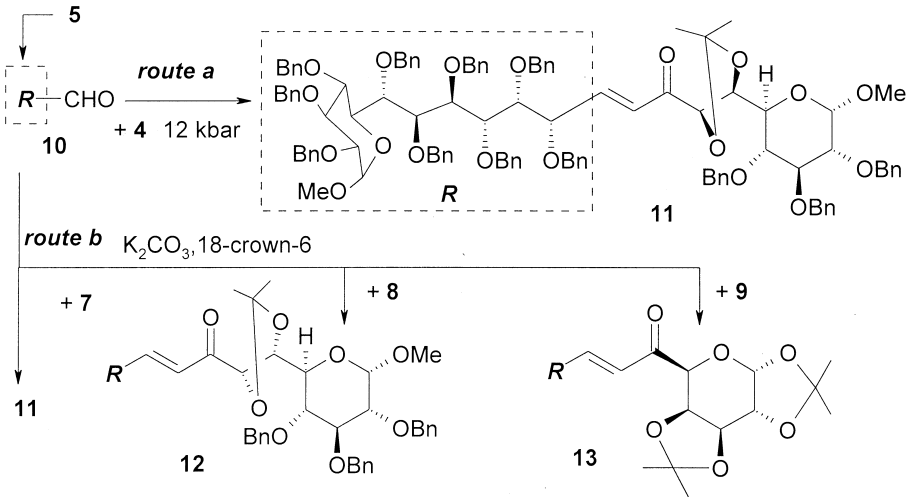
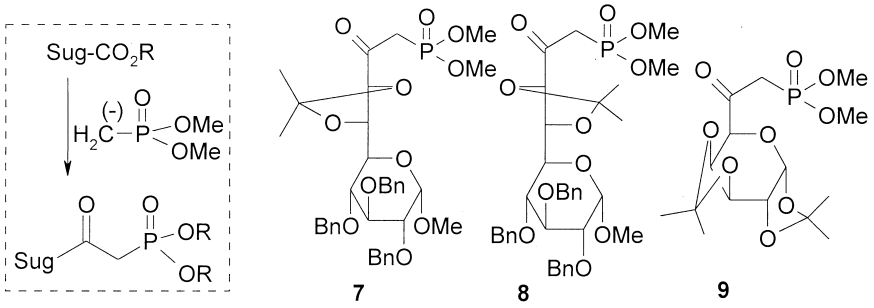
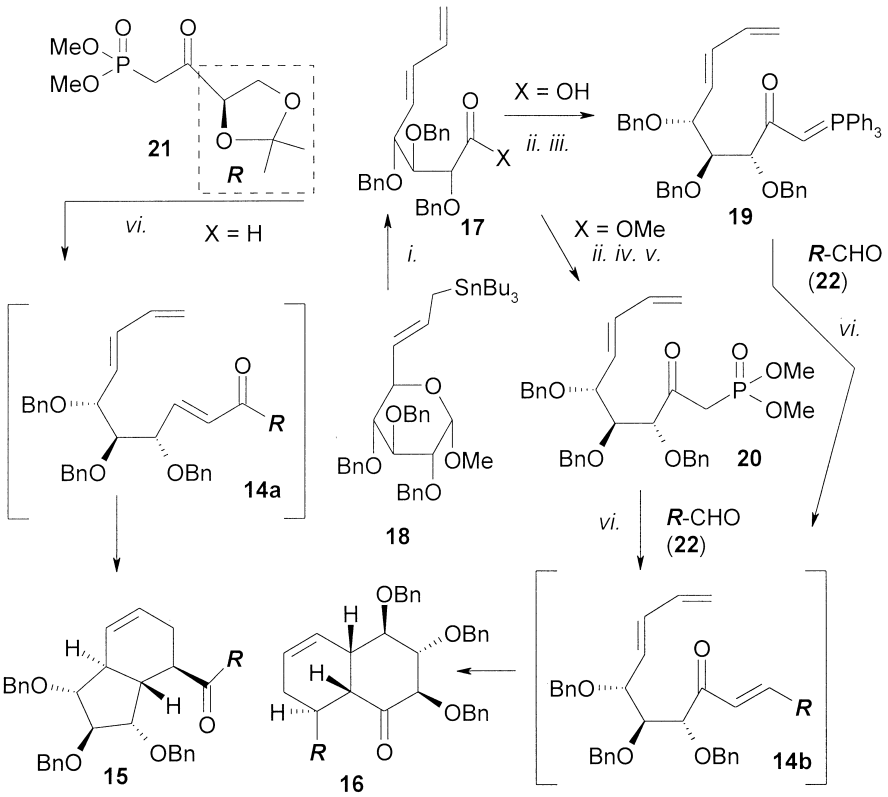


Figure 4. Synthesis of C_{21}-dialdose by coupling of a C_{12} aldehyde with a C_9-phosphorane (route a) or phosphonates (route b).



higher yields and they are more reactive towards sugar aldehydes than the corresponding phosphoranes.[13] Application of both methodologies (Wittig and Horner-Emmons) for the synthesis of the precursors of higher-carbon dialdoses (C_{21}- **11** and **12** and C_{19}- **13**) is shown in Fig. 4.

Aldehyde **10** (prepared from C_{12}-dialdose **5**) reacted with ylid **4** under 12 kbar pressure affording dialdose **11** in ca 50% yield[12] (***route a***). The same derivative **11** was also prepared by reaction of **10** with phosphonate **7** under very mild phase transfer conditions (K_2CO_3, 18-crown-6, toluene, rt; ***route b***). The latter method also allowed obtaining conveniently other sugars with a long carbon chain: **12** and **13** from the corresponding phosphonates **8** and **9**.[12]



Scheme 1. *i*. $ZnCl_2$, CH_2Cl_2, rt; *ii*. Jones' oxidation; *iii*. Im_2CO then $Ph_3P{=}CH_2$; *iv*. CH_2N_2 *v*. $^{(-)}CH_2P(O)(OMe)_2$, THF, -78 ºC; *vi*. K_2CO_3, 18-crown-6, toluene, rt.

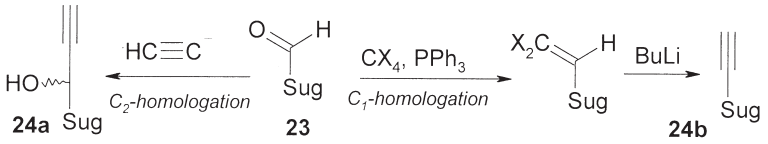


Figure 5. Conversion of aldehydo-aldoses 23 into sugar acetylenes.

Special care should be devoted to open-chain, unsaturated, higher sugar enones such as **14a**[14] and **14b**,[15] which undergo intramolecular [4+2] cyclization to perhydroindene[14] or decaline[15] derivatives (**15** and **16** respectively, Scheme 1). Enone **14a** was obtained by a Horner-Emmons reaction of unsaturated dienoaldehyde **17** (prepared by a controlled decomposition of sugar allyltin **18**[16]) with phosphonate **21**, whilst the regioisomeric compound **14b** by reaction of either phosphorane **19**[17] or phosphonate **20**[15] with 1,2-*O*-isopropylidene-D-glyceraldehyde (**22**).

2.2. Higher Carbon Dialdose Precursors by an Alkyne/Stannane Methodology

Addition of acetylene to a carbonyl group yields propargylic alcohols. When such a reaction is performed on aldehydo-aldoses (**23**, SugCHO) a C_2-homologated sugar skeleton **24a** is produced as a mixture of diastereoisomers.[18] An example of C_1-homologation (**23** → **24b**) was achieved by Corey and coworkers[19] during their work on total synthesis of *Aplasmomycin* (Fig. 5).

Both homologation methods have been applied for the preparation of a higher carbon sugar skeleton. Reaction of 6-aldehydo-1,2:3,4-di-*O*-isopropylidene-α-D-

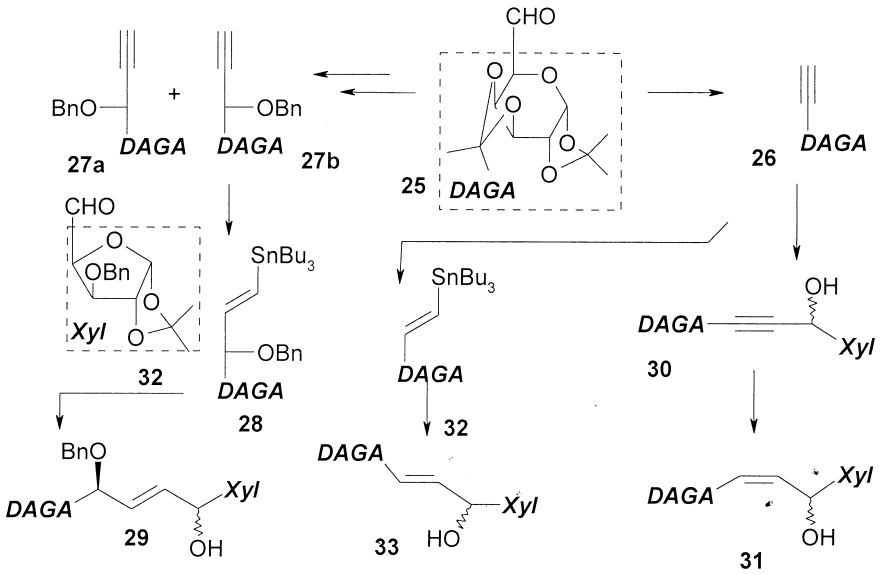


Figure 6. Application of sugar acetylenes for the synthesis of higher sugars.

galactopyranose (**25**) with acetylene anion afforded known[18] propargylic alcohols, isolated as benzyl ethers **27a** and **27b** respectively.[20] Stereoisomer **27b** was reacted with tri-*n*-butyltin hydride to yield the vinyltin derivative **28**. Replacement of tin with lithium using BuLi (this process proceeds with retention of the configuration of the double bond) and further reaction with 5-aldehydo-3-*O*-benzyl-1,2-isopropylidene-α-D-xylofuranose (**32**) furnished higher sugar precursor **29**[21] (Fig. 6).

The alkyne/vinyltin coupling method allowed us to present a general methodology for the preparation of higher sugar allylic alcohols of defined configuration of the double bond.[22] Acetylene **26** (prepared by a C_1-homologation of **25**) was converted into its anion which was reacted with aldehyde **32** to afford the propargylic alcohols **30**. Reduction of the triple bond with hydrogen over a Lindlar-type catalyst provided the *cis*-olefins **31**. Alternatively, reduction of the triple bond in **26** with Bu_3SnH followed by exchange of tin for lithium and reaction with **32** furnished the *trans* isomers **33** (Fig. 6).

2.3. Two Route Synthesis of a Higher-carbon Dialdose Precursor

Both methods described above can be combined together (Fig. 7), allowing a higher sugar skeleton (e.g. **34**) to be prepared by "two routes".

The C_3-bridge in target enone **34** is flanked by two sugar moieties: galactose and ribose. Therefore, it might be prepared starting from either sugar substrate. In ***route a***, the galactose-derived ylid **35** (prepared in 50% only from **39**) was reacted with aldehyde **36** yielding product **34** in 75% yield (ca. 38% based on **39**). In ***route b*,** the ribose substrate **36** was converted into acetylene **37** and next into vinyltin **38** (40–45% overall), which reacted further with the D-galactose aldehyde **39** to give (after oxidation of intermediate allylic alcohols) the same target **34** (in ca. 30–35% from **36**, but 75% based on **39**). The exchangeability of synthetic routes allows employing a more available (or simply cheaper) compound as substrate.[23]

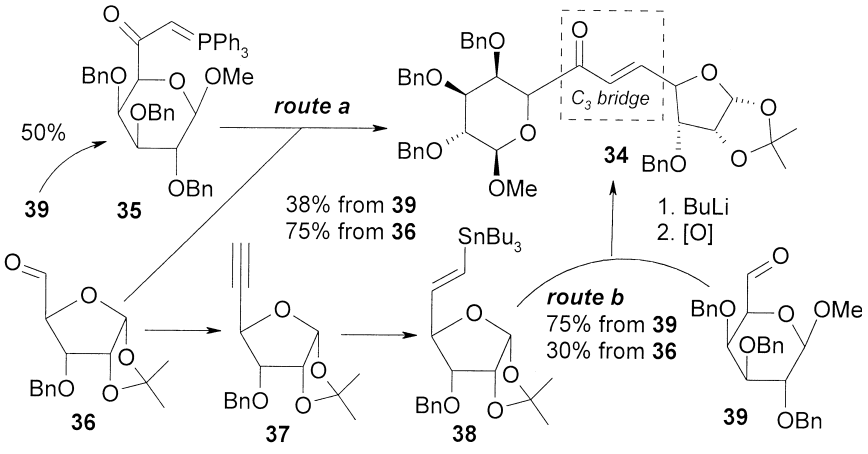


Figure 7. Economic synthesis of a higher sugar skeleton.

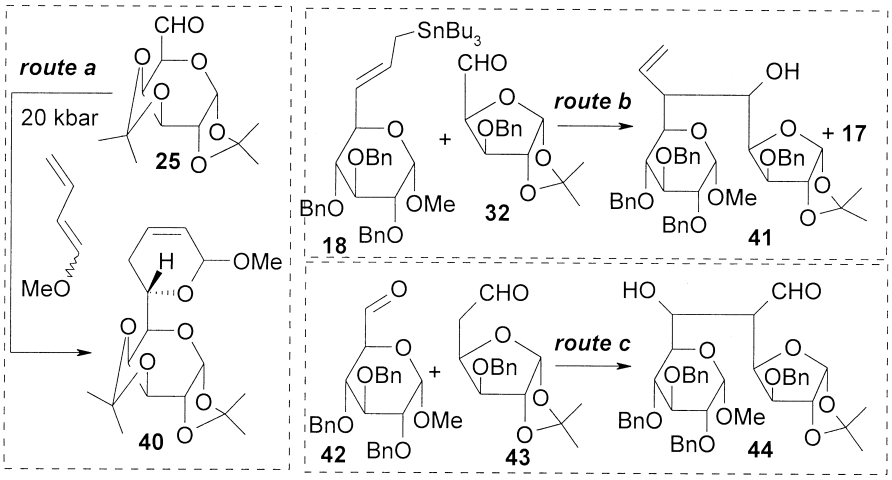


Figure 8. Preparation of a higher sugar skeleton by different routes.

2.4. Miscellaneous Methods Leading to Higher-carbon Dialdose Precursors

Three different methods (of rather limited application), other than those already described, were also applied for the synthesis of higher sugar skeletons.

In Figure 8, ***route a***, the high-pressure hetero-Diels-Alder methodology was used for the preparation of a decose precursor. Reaction of aldehyde **25** with 1-methoxy-1,3-butadiene under 20 kbar pressure afforded derivative **40** as the single isomer in good yield. At lower pressure (10 kbar) the catalyst [$Eu(fod)_3$] was used and the stereoselectivity dropped to 97:3.[24] In ***route b***, sugar allyltin **18** and aldehyde **32** were treated with $TiCl_4$ which induced a coupling leading to **41** in 55% yield (mixture of two isomers). Substantial amounts of dienoaldehyde **17** (Scheme 1), arising from decomposition of allyltin was produced.[25] In ***route c*** a directed aldol condensation of the enolate derived from **43** and aldehyde **42** led to higher sugar **44**[26] (Fig. 8).

All these methods have not found as yet a wider application for the preparation of higher sugars in our laboratory.

3. SYNTHESIS OF HIGHER CARBON SUGARS FROM THE PRECURSORS

In this section are presented the most useful methods we have employed in our laboratory for the synthesis of higher carbon sugars, i.e., functionalization of the α,β-unsaturated enone precursors. As part of this strategy, stereoselective reduction of a carbonyl function and also selective oxidation of the double bond is required (Fig. 9).

The first problem we encountered during conversion of the enones into higher sugars, was the requirement to efficiently reduce the ketone carbonyl group.

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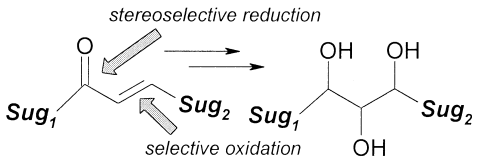


Figure 9.

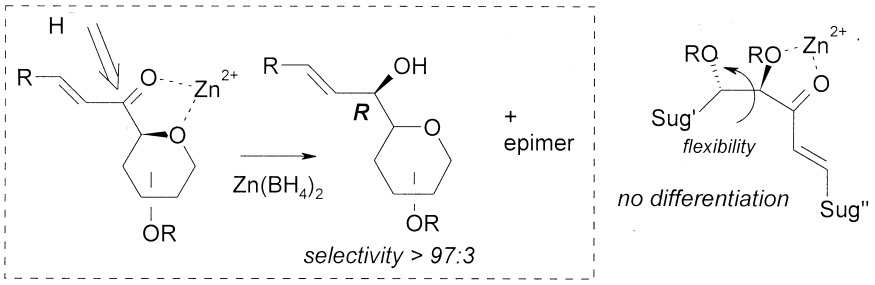


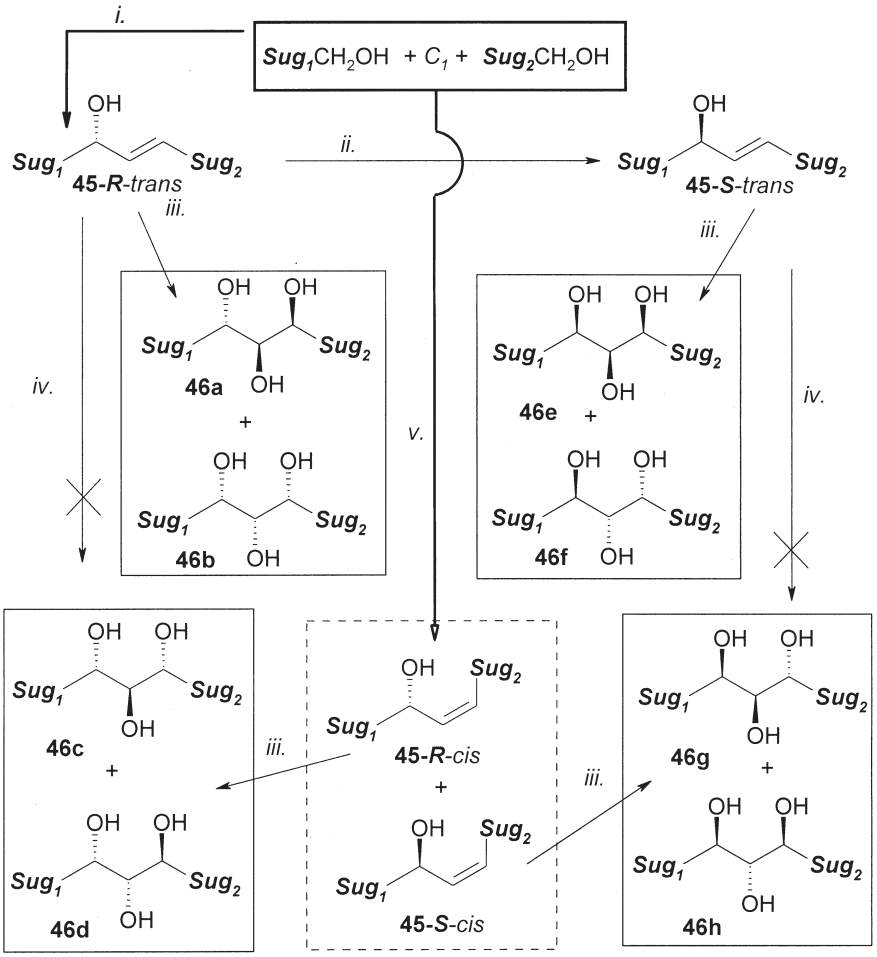
Figure 10. Model for the stereoselective reduction of higher sugar enones.

We found that reduction can be achieved with high selectivity using zinc borohydride. Reduction performed on D-sugars, afforded allylic acohols with the ***R*** configuration at the newly created chiral center[10] (Fig. 10). This result can be explained by complexation involving the carbonyl and ring oxygen atoms with zinc (with formation of a 5-membered ring chelate), fixing the conformation of the carbonyl group and favoring approach of hydride to the *si* side of the carbonyl group. The configuration at the carbinol center may-be inverted by a Mitsunobu reaction leading to the ***S***-analogs. The differentiation of the carbonyl group is much less pronounced in compounds having the carbonyl group coupled not directly to a sugar ring and a 1:1 mixture of stereoisomers is usually obtained[13] (Fig. 10).

The next problem we faced was selective oxidation of the allylic alcohol double bond to the corresponding triol. Bis-hydroxylation of the allylic bridge of a higher sugar skeleton **45** can result in formation of eight (**46a–46h**) stereoisomeric triols (Fig. 11).

Coupling of two monosaccharide sub-units *via* a Wittig-type methodology (see **2.1.**) afforded a higher sugar enone* in which the carbonyl function was stereoselectively reduced with zinc borohydride to allylic alcohol **45-*R*-*trans***. *Cis*-hydroxylation of the double bond with OsO_4 proceeded according to Kishi's rule and gave triols **46a** and **46b**. The remaining two triols from the ***R***-series (**46c,d**) might eventually be prepared by epoxidation of the double bond in **45-*R*-*trans*** followed by regioselective opening of the oxirane ring. However, both these processes are hardly applicable for higher sugar allylic alcohols such as **45**.[27] Therefore, triols

* The same enone might be also prepared by oxidation of allylic alcohols (e.g. **33**, Fig. 6) resulting from alkyne/stannane methodology (see chapter **2.2.**).



i. The Wittig approach followed by stereoselective reduction of the C=O group; *ii.* Mitsunobu inversion at the carbinol center; *iii.* OsO_4 / NMO; *iv.* epoxidation followed by opening of the oxirane ring; *v.* the alkyne approach followed by reduction of the triple bond over Lindlar catalyst.

Figure 11. Functionalization of the allylic bridge in higher sugar skeketons.

46c,d were prepared by an alternative route involving osmylation of the **45-*R*-*cis*** allylic alcohol (obtained *via* alkyne methodology, see **2.2.**).

The remaining four triols, **46e-h**, were prepared analogously from allylic alcohols **45-*S*-*trans*** and **45-*S*-*cis***.[28]

4. ADDITIONAL EXAMPLES OF SYNTHESES OF HIGHER CARBON SUGARS

4.1. Stereoselective Synthesis of Pentadecadialdose

The synthesis of pentadecadialdose **51**[29] was initiated from the readily available acetylene **27a** (see **2.2.**) and hepto-dialdoside **47** (Fig. 12). The anion generated from **27a** with BuLi reacted with aldehyde **47** to afford a 2:1 mixture of two stereoisomeric propargylic alcohols **48** and **49** in 50% yield.[20] The alcohols were interconvertible by a Mitsunobu reaction.

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Compound **49** was benzylated under standard conditions and the triple bond was reduced with H_2 over $Pd/BaSO_4$ to a *cis*-double bond (**50**). This double bond proved to be extremely resistant towards osmylation and the *cis*-hydroxylation of **50** could be performed only using an excess of osmium tetraoxide in pyridine (in two weeks) leading to both stereoisomeric diols **51a** and **51b** with very low (ca 2:1) selectivity. The configuration of the main C_{15}–dialdose isomer[29] (**51a**) was consistent with Kishi's rule.

4.2. Stereoselective Synthesis of a C_{12}-alditol

The elaborated methodology allowed for the first stereocontrolled synthesis of an alditol having more than 10 carbon atoms in the chain[30] (Fig. 13). Synthesis was initiated from the D-*gluco*-configurated phosphonate **52** and the D-*arabino*-aldehyde **53**. The Horner-Emmons reactions of the two reactants under mild basic conditions (K_2CO_3, 18-crown-6, toluene, room temp) led to higher sugar enone **54** in 75% yield. Stereoselective reduction of the carbonyl group with zinc borohydride afforded alcohol **55** as a single isomer. Protection of the hydroxy group as a benzyl ether (**55** → **56**), followed by osmylation of the double bond afforded higher sugar diol **57** with very high stereo-selectivity (ratio **57** : **57a** = 96:4). This result was not particularly surprising, since – according to Kishi's rule – attack of osmium tetraoxide should proceed *anti* to the hydroxy (or alkoxy) function(s). In compound **56** the stereochemistry of both oxygen functions flanking the double favor formation of the diol **57**, the dominant product formed.

Diol **57** was benzylated to give **58**, the acetonide protecting groups were removed under acidic aqueous conditions, and the resulting tetraol was benzylated to

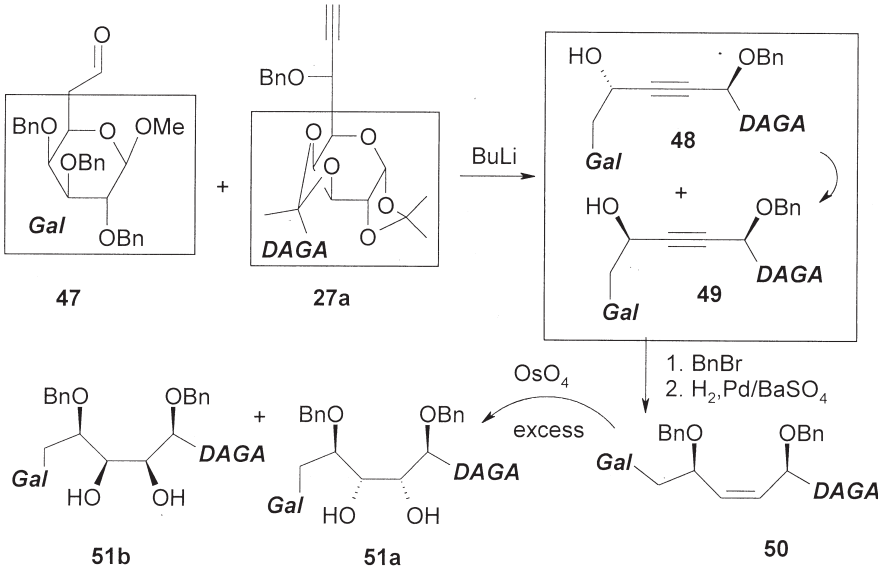

Figure 12. Synthesis of a pentadecadialdose from $C_8{}^+C_7$ sub-units.

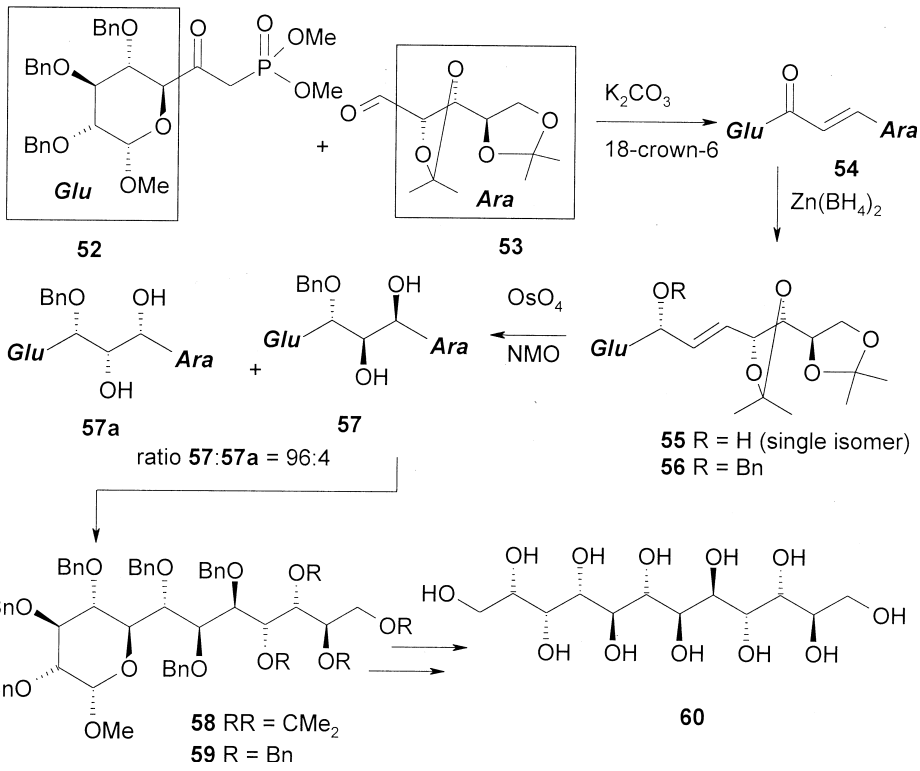

Figure 13. Stereoselective synthesis of a dodecitol.

afford **59**. Hydrolysis of the methyl glycoside, reduction of resulting hemiacetal and final deprotection furnished the dodecitol **60**. This compound could be easily prepared in a 0.5 g scale.

5. CONCLUSION: SCOPE AND LIMITATION OF THE METHODOLOGY

The synthesis of higher carbon di-aldoses can be accomplished by a coupling of two suitably activated monosaccharide sub-units *via* their terminal C-atoms. They may be connected either directly or by insertion of an additional carbon atom(s) to give a precursor, which is further converted into a higher monosaccharide. The best methods we have found for connection of two sugar sub-units are undoubtedly the Wittig-type coupling and the alkyne/stannane methodology.

Coupling of two sugars *via* the Wittig reaction requires conversion of one sub-unit into a stabilized phosphorane. This reaction is rather capricious; the yields of the ylids are not particularly high (ca. 50%) and higher ylids (having at least 9 carbon atoms) are completely unreactive towards aldehydes under the normal conditions, although they react under high pressure conditions. The phosphonate methodology (the Horner-Emmons approach) is more convenient, since the sugar

P→O ylids are usually prepared in much higher yields and they are more reactive towards sugar aldehydes than the corresponding phosphoranes.

An alternative to the Wittig or Horner-Emmons routes is an approach based on sugar acetylenes, which allows for convenient preparation of higher sugar allylic alcohols of the desired double bond configuration. The allylic bridge in higher sugar enones might be functionalized with a high degree of stereoselectivity. Reduction of a carbonyl function with zinc borohydride gives exclusively allylic alcohols with the ***R*** configuration at the newly created chiral center. This method, however, is limited thus far only to systems in which the carbonyl function is placed at the α-position to a sugar ring. Oxidation of the double bond of resulting allylic alcohols can be done conveniently only by osmylation. Epoxidation, and subsequent opening of the oxirane ring is not as yet a predictable process.

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