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The Applications of Lewis Acids in Carbohydrate Chemistry

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The review gives a systematic account of the results of studies on the use of Lewis acids as catalysts of the chemical reactions of carbohydrates including polysaccharides. The data concerning the effect of Lewis acids have been grouped. in terms of the types of chemical reactions characteristic of the given class. The scope and certain limitations of their practical applications are indicated.
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I. INTRODUCTION

Catalysis by acids and bases of the Brønsted type is widely used in carbohydrate chemistry[1-3]. Systematic studies on the kinetics of reactions under the conditions of homogeneous acid–base catalysis established many qualitative and quantitative rules governing the influence of the acidity of the medium on the kinetic and activation parameters, the equilibrium, and the mechanisms of many reactions of simple sugars (see, for example, Refs. 4–10). The study of the mechanisms of these reactions promoted in its turn the determination of the fundamental rules of acid–base catalysis and the development of physical organic chemistry[11-14].

The situation is somewhat different as regards the applications of Lewis acids (LA) in carbohydrate chemistry. One cannot say that agents of this type have been altogether disregarded by chemists specialising in the field of carbohydrates. Thus, as early as 1892 Stockhausen and Gatterman[15,16], and then in 1926 Kunz and Hudson[17], drew attention to the formation of the disaccharide chloroderivative when lactose octa-acetate is treated with a solution of aluminium chloride in chloroform. It was shown that the acetyl group at the glycosidic centre ($C_{(1)}$) had been substituted by chlorine. The crystalline product isolated from the reaction mixture was called neolactose. In subsequent years, research workers frequently used Lewis acids in order to elucidate the scope of their applications in preparative sugar chemistry. In many instances, these studies led to a significant development of the methods in carbohydrate chemistry. As regards the theoretical aspect of catalysis by Lewis acids, the problem has not been the subject of any kind of systematic investigation. It is useful to survey the available literature data and to outline the principal trends of the development of Lewis acid catalysis as a method in carbohydrate chemistry.

In the vast majority of studies, compounds of the type MX_n, where X is a halogen and M the central atom functioning as an acceptor of electron pairs, have been used as Lewis acids. Attempts have been frequently made to arrange systematically compounds of this type in terms of their acid and catalytic functions[18-20], but they did not lead to the development of a universal acidity scale. The relative acidity scale of MX_n, obtained on the basis of the valence interactions of the Lewis acid with a base in terms of measurements of the equilibrium constants for these reactions[19], is the most successful:

$$MX_n + yB \rightleftarrows MX_nB_y \quad .$$

This scale in general agrees well with experimental data (for example with the chemical shifts of the α-protons in the ^{1}H NMR spectra of a series of oxygen compounds coordinated to Lewis acids)[20]. By analogy with the Hammett function H_0, Moiseev[21] proposed for variable-valence metal ions an aprotic acidity function θM, which may be used to interpret processes involving the π-complexes of ions and unsaturated compounds.

Quantum-chemical calculations have shown that, in estimating the Lewis acidity, one must take into account not only the electronic structure of the central atom but also the steric configuration of the Lewis acid complex with the base[22,23]. On the whole, the problem of the acidity spectrum of Lewis acids is still far from being fully solved, which is a serious obstacle to the development of a quantitative theory.

As in protic catalysis, the mechanisms of the Lewis catalysis of reactions can be represented by schemes providing for the interaction of the central atom of the Lewis acid with the heteroatoms of the carbohydrate molecule, involving the formation of a coordinate of covalent bond. However, with the exception of isolated individual studies[24-28], the experimental research devoted to problems of the formation of complexes by carbohydrates with Lewis acids is still insufficient to infer with any certainty the role of coordination compounds in the catalysis of the reactions of sugars. The problem of the possible activation of molecules by the protic acid produced at the stage in which the Lewis acid is coordinated to the heteroatom (for example $HB + MX_4 \rightarrow HB.MX_4 \rightarrow B - MX_3 + HX$) has not been considered in the literature at all. Nevertheless such a possibility must be taken into account in the analysis of the mechanisms of Lewis catalysis, particularly when the reactions are carried out in the presence of traces of water. In the present review, the literature data have been grouped in terms of their relevance to the characteristic reactions of simple sugars and polysaccharides.

II. ISOMERIC TRANSFORMATIONS OF *O*-GLYCOSIDES

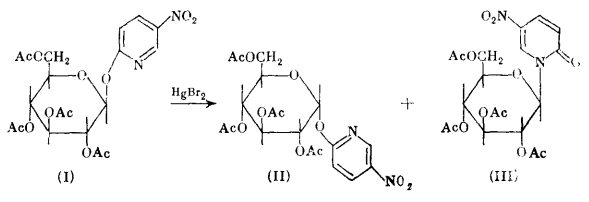
In contrast to monosaccharides and *N*-glycosides, *O*-glycosides are known[1] not to undergo anomerisation in moderately acidic aqueous solutions. Within the framework of general ideas on catalysis by Brønsted acids[6,13], the stability of the *O*-glycoside system can be accounted for by the low basicity of the proton acceptors—the ring and glycosidic oxygen atoms—responsible for the acid activation of the molecule. Appreciable protonation of these centres can be observed only in concentrated acid solutions, but in this case the anomerisation phenomenon is masked by the rapid acid hydrolysis of the *O*-glycosidic linkage. Anomerisation uncomplicated by the hydrolysis of the *O*-glycoside system can be observed in non-aqueous media, for example, in an acid methanolic solution of methyl β-D-glucopyranoside[29] or in inert organic solvents containing added Lewis acids.

This phenomenon was first observed by Pacsu[30-32] on refluxing briefly methyl tetra-*O*-acetyl-β-glucoside, cyclohexyl tetra-*O*-acetyl-β-glucoside, and methyl hepta-*O*-acetyl-β-cellobioside in the presence of $TiCl_4$ or $SnCl_4$ in dry chloroform. Fully acetylated and benzoylated sugars are also anomerised under the influence of BF_3 in chloroform, $HgBr_2$ in benzene, and many other Lewis acids in non-aqueous media[33-39]. In contrast to alkyl derivatives, glycosides with aromatic *O*-aglycones do not anomerise appreciably under analogous conditions[40]. The introduction of an electron-accepting aglycone suppresses to a large extent the anomerisation and at the same time increases the probability of the dissociation of the glycosidic linkage and the halogenation of the glycosidic atom. Anomerisation under the influence of non-aqueous $TiCl_4$ solutions is used nowadays in the preparative chemistry of carbohydrates in order to obtain anomeric forms of *O*-glycosides, which are otherwise difficult to synthesise (see, for example, Refs. 39 and 41).

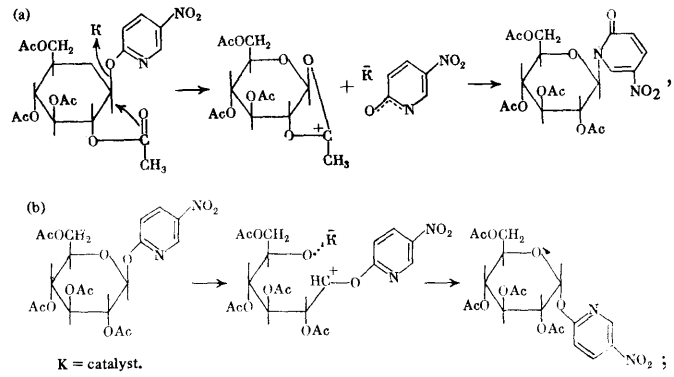
There exist contradictory views concerning the anomerisation mechanism which, incidentally, may be said also of other reactions of the glycosidic centre[5]. The problem of the detailed mechanisms of the catalysis of carbohydrate reactions is one of the most obscure in sugar chemistry. This does not involve the kinetic description of the reaction systems but is concerned with the selection of the most probable scheme for the coordination of the catalytic agent to the active centres and the mechanism of the subsequent reaction of the activated molecules.

According to Lindberg[34], anomerisation involves the opening of the carbohydrate ring with formation and subsequent cyclisation of an intermediate. The scheme of Lemieux and Shyluk[40] provides for the coordination of the catalyst to both ring and glycosidic oxygen atoms and for the possibility of reaction with heterolysis of the glycosidic or inner hemiacetal linkage, but without the formation of kinetically detectable ions.

The anomerisation of the *O*-glycoside (I) in the presence of $HgBr_2$ is accompanied by an intramolecular rearrangement (*ON*-transglycosylation), which results in the formation of the β-anomer of the *N*-glycoside (III)[42]:



The above rearrangement under the influence of Lewis acids has been studied in a number of investigations[38,42-44]. The proposed mechanisms of the catalysis presuppose two possible types of coordination of the Lewis acid—with the glycosidic (a) or ring (b) oxygen atoms, the first of which leads to intramolecular *ON*-trans glycosylation and the second to the anomerisation of the initial *O*-glycoside:



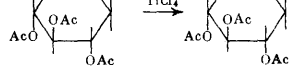
The activities of Lewis acids in the anomerisation reaction (b) increase in the following sequence: $TiCl_4 < SbCl_5 < SnCl_4 < CdCl_2 < ZnBr_2 < HgBr_2$.[38]

Lewis acids are apparently capable of inducing the epimerisation reaction in carbohydrates. For example, D-mannose-6-phosphate epimerises in an acetate buffer at pH 6 and 50°C in the presence of Fe^{3+}, Cr^{3+}, Al^{3+}, etc. to D-fructose-6-phosphate and D-glucose-6-phosphate[45]. The authors suggest that the ability of metal ions to catalyse the isomerisation reaction is determined by their properties as Lewis acids; the selectivity of the reaction does not in essence depend on the catalyst: D-fructose-6-phosphate is formed in all cases.

Another type of isomerisation occurring under the influence of Lewis acids is the Amadori reaction, the kinetics of which have been investigated in the presence of $ZnCl_2$ in anhydrous dioxan[46].

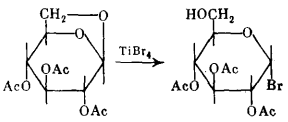
III. THE FORMATION OF GLYCOSYL HALIDES

The halides of Group IV elements behave in relation to carbohydrates not only as catalysts but also as effective halogenating agents—a factor which must be always borne in mind in the analysis of the mechanisms of Lewis catalysis. When fully or partly acetylated sugars are introduced into the reaction in non-polar or weakly polar media, mainly the substituent at $C_{(1)}$ is replaced by the halogen[15-17]. A method for the synthesis of glycosyl halides, whereby one can obtain unstable anomeric forms of glycosyl halides, has been developed on this basis[47,48]. For example, tetra-*O*-acetyl-β-D-glucopyranosyl chloride can be obtained in a satisfactory yield after a brief treatment of β-D-glucose with a benzene solution of $TiCl_4$:

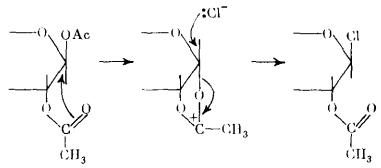


On further treatment of the β-anomer with $TiCl_4$, the former undergoes anomerisation with formation of the α-anomer, which is thermodynamically more stable under the conditions of Lewis catalysis. Anhydrous $AlCl_3$ in

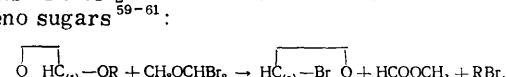
chloroform has a similar effect[47,49-51]. Treatment of tri-*O*-acetyl-laevoglucosan with a $TiBr_4$ solution causes the formation of 2,3,4-tri-*O*-acetyl-α-glucosyl bromide[52]:



$TiCl_4$ has a similar effect on the hexa-*O*-acetyl derivatives of 1,6-anhydrocellobiose[53] and 1,6-anhydromaltose[54]. When hydrogen halides are used as the halogenating agents, the reaction is completed by the formation of a mixture of anomeric forms of the glycosyl halides in which the more stable α-anomer predominates. In contrast to this, the halogenation reaction involving the halides of Group III and IV elements is controlled by kinetic factors and may be arrested at the stage involving the formation of the β-anomers. The mechanism of the substitution of the aglycone for a halogen in acetyl derivatives of sugars may be represented by a scheme involving the participation of the neighbouring acetyl group[55,56]:



The effect of neighbouring group participation plays an important role in the stereochemical pathways of the reactions of the glycosidic centre[1] and its investigation is essential for the development of methods of stereospecific synthesis of sugar derivatives. For example, it has been established that, in the mercaptanolysis of the penta-*O*-acetyl derivatives of glucose and mannose in the presence of $ZnCl_2$, the reactivity of the β-anomers is much greater than that of the α-anomeric forms[57]. Measurements of the rates of exchange of the acetoxy-group at $C_{(1)}$ in the penta-*O*-acetyl derivatives of glucose and mannose with tin trichloride acetate in the presence of $SnCl_4$ in chloroform showed that the 1,2-*trans*-anomeric forms react much faster than the 1,2-*cis*-anomers[58]. These observations permit the conclusion that there is an intramolecular nucleophilic attack by the acetyl group at $C_{(2)}$ on the glycosidic centre, which weakens the glycosidic linkage (intramolecular nucleophilic catalysis). Acetylated derivatives of pentoses, hexoses, and disaccharides as well as partly acetylated sugars with a free glycosidic hydroxyl readily react with α-halogenoethers in the presence of catalytic amounts of $ZnCl_2$ in chloroform with formation of acetohalogeno sugars[59-61]:

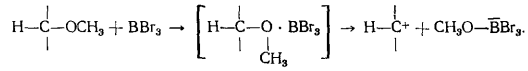


The yields of α-bromo-derivatives of tetra- and penta-*O*-acetylmonosaccharides vary in the range 50–60%.[59]

IV. THE DISSOCIATION AND FORMATION OF CARBON–OXYGEN BONDS

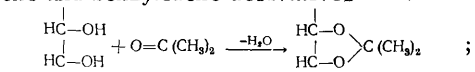
1. Chemical Reactions involving the Hydroxy-Groups

An effective low-temperature method for the demethylation of sugar derivatives under the influence of boron halides has been developed[62-66]. The same catalysts may also be used for deacetylation and the removal of the acetal group. For example, for the exhaustive demethylation of 2,3,4,6-tetra-*O*-methylglucopyranose, it is sufficient to keep the ether in methylene chloride in the presence of BBr_3 for 30 min at −80°C.[49] The use of BCl_3 under the same conditions leads to only partial demethylation (while hydrogen chloride dissociates only the glycosidic linkage and does not affect the ether linkages[65]) and the elimination of the methyl group may be accompanied by epimerisation at the carbon atom undergoing *O*-demethylation[67]. Monosaccharides are fully resistant to the action of BCl_3, with the exception of D-fructose and L-sorbose, the demethylation of which is accompanied by the formation of appreciable amounts of 5-hydroxymethylfurfural[66]. It has been noted that, in contrast to BBr_3, BCl_3 does not cleave the glycosidic linkages in disaccharides. Polycondensation with formation of di- and oligo-saccharides is also possible in the demethylation process[63]. There is no information in the literature about the mechanism of the demethylation reactions. It is suggested that the first stage involves the heterolysis of the carbon–oxygen bond in accordance with the scheme[64]

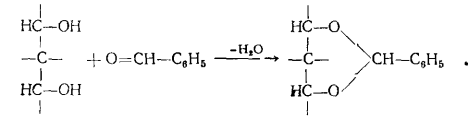


Lewis acids are widely used in the chemistry of carbohydrates, including polysaccharides, in order to synthesise ethers, including the selective protection of hydroxy-groups. CH_2N_2 + BF_3 (or BF_3 etherate) is a convenient methylating system for the synthesis of methyl ethers of sugars[68-72]. For example, a method has been developed on this basis for the synthesis of 2-*O*-methyl-D-galactose, involving the treatment of 4,6-*O*-benzylidene-3-*O*-benzoyl-β-benzyl-D-galactopyranoside with an excess of CH_2N_2 in solution in methylene chloride in the presence of BF_3 etherate, followed by debenzoylation under the influence of lithium tetrahydro-aluminate and hydrogenolysis over palladised charcoal[69].

Much attention has been devoted in carbohydrate chemistry to anhydrous zinc chloride as the catalyst of the selective protection of glycol OH groups by the formation of isopropylidene and benzylidene derivatives[73-75]:

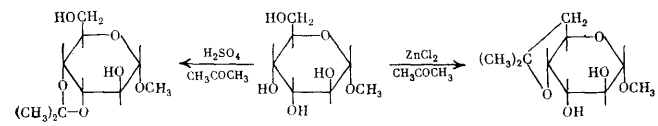


(1)



(2)

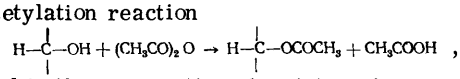
Both strong inorganic acids and $ZnCl_2$ can be used in the synthesis of the isopropylidene derivatives (1)[75-77]. On the other hand, in order to obtain benzylidene derivatives (2), mainly $ZnCl_2$ is used[74,78-82]. When the isopropylidene protecting group is introduced in the presence of $ZnCl_2$, the six-membered *m*-dioxan ring is formed preferentially. It is less stable than the five-membered dioxolan ring formed in the reaction catalysed by protic acids[83]:



A similar tendency has been observed also in catalysis by zinc chloride of the reaction involving the formation of benzylidene derivatives[74,78,84]. Incidentally, this rule is

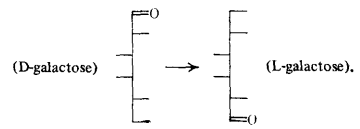
not entirely rigorous. The structure of the cyclic protecting group depends not only on the nature of the catalyst, but also on the form in which the initial monosaccharide participates in the reaction—open-chain or cyclic. In particular, when *O*-glycosides with the cyclic structure are substituted by acetone, the isopropylidene protecting group gives rise to *m*-dioxan and dioxolan rings. On the other hand, the isopropylidene protecting group enters into the open-chain forms of monosaccharides mainly as the dioxolan fragment.

The acetylation reaction



widely used in the preparative chemistry of sugars, is catalysed by both acid and basic catalysts. Among the Lewis acids used in this reaction, $ZnCl_2$ is most common. Fructose[85,86], salts of aldonic acids[87], cellulose[88], and other derivatives have been successfully acetylated in the presence of $ZnCl_2$. The addition of BF_3 accelerates the acetylation of uronic acids by acetic anhydride[51,89]. As in other reactions of sugars, the anomerisation of partly or fully acetylated forms is a complicating factor. In the presence of acid catalysts, the equilibrium shifts towards the preferential accumulation of the α-anomer as the temperature is raised. $ZnCl_2$ can therefore be used to obtain the α-anomer directly during acetylation with a mixture of acetic anhydride and acetic acid. For example, in order to obtain the α-anomer of penta-*O*-acetylgalactopyranose, it is sufficient to treat the β-anomer with the acetylating mixture in the presence of $ZnCl_2$.[90,91]

We may note that the D–L isomerisation of a galactose derivative has been achieved by Micheel and coworkers[92,93] on the basis of the acetylation reaction in the presence of $ZnCl_2$ via the mechanism

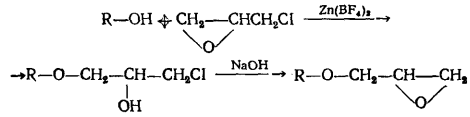


i.e. by converting the 6-hydroxy-group into a formyl group and the glycosidic centre into a primary alcohol fragment. They showed that treatment of 2,3,4,5-tetra-*O*-acetyl-6-tosyl-*al*-D-galactose with zinc chloride in acetic anhydride leads to the formation of a racemic mixture of the D- and L-forms of hepta-*O*-acetylgalactose. After 30 years, Micheel returned to the study of this reaction and confirmed with the aid of $C_{(1)}$-labelled galactose the validity of the fundamental isomerisation mechanism[94].

It has been shown that BF_3 in anhydrous dioxan catalyses the formation of methyl 4,6-*O*-methylene-D-glycopyranosides on reaction of methyl glycopyranosides with formaldehyde[95]. Furthermore, BF_3 and $SbCl_5$ in methylene chloride catalyse the addition of glycosidic fragments to the free OH groups of acetylcellulose when the latter reacts with *O*-protected thio-, *O*-, and *N*-glycosides[96]. The degree of substitution varies in the range 0.1–0.47 depending on the nature of the glycosylating agent. Compared with BF_3 and $SbCl_5$, Lewis acids such as $AlCl_3$, $AlBr_3$, $TiCl_4$, and $ZnCl_2$ proved to be less effective agents in the substitution reaction.

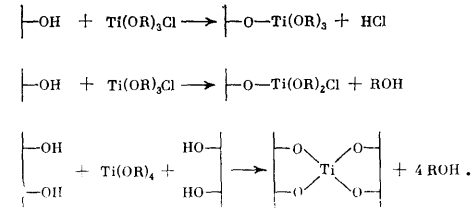
Lewis acids are also used in the chemistry of polysaccharides, particularly cellulose, in order to synthesise its alkyl and acyl derivatives. Comparative studies have shown that the Lewis acids can be arranged in the following sequence in terms of their catalytic activity in the formation of cellulose ethers and esters[97]: $FeCl_3 > SbCl_5 > AlCl_3 > TiCl_4 > SnCl_4 > ZnCl_2 > BF_3.O(C_2H_5)_2 > HgCl_2$.

The influence of Lewis acids on the reactions of cellulose, acetylcellulose cellulosedialdehyde, and carboxymethylcellulose with the epoxy-derivative of butadiene has been studied[98]. It has been shown that the reaction of cellulose with chloromethyloxiran in the presence of zinc tetrafluoroborate followed by treatment of the product with a dilute solution of NaOH leads to the formation of a cellulose ether containing a free epoxy-group[99]:



However, comparative studies of the influence of the addition of acids and bases on the interaction of cellulose with various aromatic mono- and bi-functional epoxy-derivatives have shown that Lewis acids are nevertheless less suitable than alkaline agents for the preparation of cellulose ethers, since they initiate many side reactions arising owing to the degradation of the macromolecules[100].

The interaction of $TiCl_4$, alkoxytitanates, and titanate orthoesters with polyols, unsubstituted sugars, and cellulose leads to the partial or complete substitution of the chlorine atoms and alkoxy-groups and the formation of Ti–O–C linkages as a result of the exchange interaction with the free OH groups of the carbohydrate chains[101,102] for example:



Ammonia, pyridine, formamide, or dimethylformamide are used as the hydrogen chloride acceptors. In contrast to $TiCl_4$ complexes with acetylated sugars, titanium-containing sugar and cellulose ethers [and esters?] are resistant to hydrolysis in weakly alkaline and neutral media.

Lewis acids exhibit a catalytic effect in the transesterification of cellulose nitrates by carboxylic acid chlorides[103–106]. The nitrogen content in the substitution product varies approximately exponentially with catalyst concentration at a fixed instant. For example, in the reaction of cellulose nitrate and acetyl chloride at 20°C, the dependence of the nitrogen content on the $AlCl_3$ concentration is of the following form 60 min after the start of the reaction[106]:

$$\ln [N],\ (\%) = 2.50 - 0.25\,[AlCl_3],\quad r = 0.98.$$

The possible mechanisms of this reaction have been analysed[103].

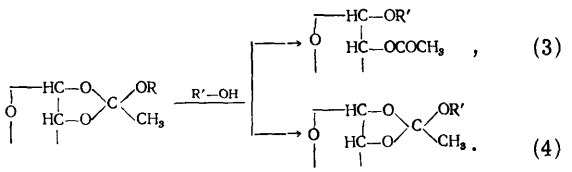
2. The Formation and Dissociation of Glycosidic Linkages

The synthesis of *N*-glycosides with strongly and moderately basic aglycones does not as a rule present special difficulties[107]. The problem of finding effective (particularly stereoselective) methods for the synthesis of glycosides with weakly basic aglycones (in particular *O*-glycosides[1]) constitutes a more urgent problem. In the search for these methods, the influence of Lewis acids has been frequently studied. Thus it has been suggested[108] that $ZnCl_2$ be used to synthesise thioglycosides, while in another

study[109] anhydrous $AlCl_3$ was proposed for the synthesis of *O*-arylglycosides by the Helferich method. However, the greatest success has been achieved in the employment of mercury salts as initiators of the formation of glycosidic linkages[50,56,110-112].

The Zemplen–Helferich version[113,114] of the Koenigs–Knorr *O*-glycosylation method, according to which mercury acetate or cyanide is added to the organic solvent (benzene, chloroform, nitromethane, acetonitrile) in order to obtain *O*-alkyl glycosides, has been widely used in laboratory practice. These additives are believed to play the role of acceptors of hydrogen chloride, which is eliminated from the initial acyl halides, although one cannot rule out the possibility that they also exhibit the catalytic functions characteristic of Lewis acids. Among individual reports, one may mention the catalysis by mercury chloride of the formation of *O*-glycosidic linkages in 2-deoxysugar derivatives[115-117].

Kochetkov and coworkers[118,119] proposed and subsequently developed significantly[120,124] a method for the synthesis of *O*-glycosides as a result of the interaction of catalytic amounts of $HgBr_2$:



(3)

(4)

The mode of reaction depends significantly on the nature of the solvent and the amount of catalyst. Thus, the transesterification [reaction (4)] takes place preferentially in dichloroethane with formation of a new orthoester. On the other hand, when nitromethane is used and at $HgBr_2$ concentrations not exceeding 8×10^{-3} mole per mole of the initial orthoester, the reaction is directed towards glycosylation [reaction (3)].[125] Certain disaccharides and polysaccharides have been obtained by this method[126-128].

One of the highly promising trends in carbohydrate chemistry involves studies on the development of specific methods for the synthesis of polysaccharides[1,129]. The vigorous development of research on this problem is associated with the task of finding new biopolymers—blood plasma substitutes, anticoagulants, etc. As a rule the acid-catalysed polycondensation of simple sugars with unsubstituted OH groups leads to the formation of oligo- and poly-saccharides with different sets of hemiacetal and ether linkages between the monosaccharide units and a disordered branched structure. Lewis acids have been used to accelerate the synthesis of polysaccharides only in very few investigations. One may mention the polymerisation of 1,6-anhydroglucose in the presence of boron, aluminium, and iron halides[130], the polymerisation of 1,4-anhydro-2,3,6-tri-*O*-benzylglucopyranoside in the presence of boron trifluoride etherate and antimony and phosphorous pentafluorides[131], and the copolymerisation of *O*-substituted derivatives of 1,6-anhydroglucose and 1,6-anhydromaltose under the influence of PF_5 in methylene chloride at low temperatures[132]. Tetra-*O*-acetyl-β-D-mannopyranoside polymerises under the influence of $ZnCl_2$ with formation of oligomers[133]. An approximately 10% yield of a linear polymer with a regular structure has been obtained by treating 2,3,4,2′,3′,4′-hexa-*O*-acetyl-6-t-butylmelibiosyl chloride with mercury cyanide in boiling nitromethane and subsequent Zemplen deacetylation[134].

The orthoester method of forming *O*-glycosidic linkages is promising for the specific synthesis of oligo- and polysaccharides[126,127]. Prolonged treatment of partly substituted sugar orthoesters (having one free OH group) with small amounts of $HgBr_2$ in boiling nitromethane leads to the formation of regular polysaccharides. In particular, a galactoglucan—a heteropolysaccharide consisting of alternating α-galactopyranose and α-glucopyranose units linked by 1,6-bonds (molecular weight approximately 1500)—and an arabinan—a polysaccharide made up of α-L-arabinofuranose with α-glycosidic linkages (molecular weight approximately 8000)—have been obtained in this way[126].

There is comparatively little information about the catalytic activity of Lewis acids in reactions involving the dissociation of *O*-glycosidic linkages. Kinetic studies[135-137] demonstrated a pronounced destructive action of $AlCl_3$, $TiCl_4$, and $SnCl_4$ in non-polar solvents in relation to the acetal linkages of cellulose. During the first 5–10 min from the start of the reaction, the average degree of polymerisation (DP_{av}) already reaches its lowest value (150–200) and remains constant virtually without change even after 10 days of treatment with the degrading agent. Under these conditions, temperature does not have a significant influence on the process kinetics. Thus, when cotton cellulose is kept in 0.1% $AlCl_3$ solution in dry carbon tetrachloride for 5 min, DP_{av} falls from 2200 to 200 and in the resulting specimen there are no macromolecules with $DP > 200$ whatsoever. X-Ray diffraction analysis of the degraded specimens showed that the positions and relative intensities of the diffraction reflections remain the same as in the initial cellulose. This result can be explained by the fact that mainly the glycosidic linkages in the structurally disordered regions, which do not give rise to an intrinsic diffraction pattern, are degraded. On the other hand, the ordered part of the cellulose fibre retains its supermolecular structure during treatment with the degrading agent. There is virtually no decomposition from the ends of the chains.

The solvent in which the process is carried out has a marked influence on the degradation kinetics[138]. It has been shown that the degree of degradation of cellulose with 0.1 and 1% solutions of Lewis acids at 20°C diminishes regularly over a period of 5–60 min with increase of the dielectric constant ε of the non-aqueous solvent. The nature of the change of the average degree of polymerisation as a function of ε shows that the subsequent electrostatic interaction plays a significant role together with the donor–acceptor interaction via the lone electron pair of the solvent molecule and the vacant orbital of the central atom of the Lewis acid. For example, the influence of organic solvents with low dielectric constants ($\varepsilon < 12$) on the degree of degradation of cellulose specimens by 1% $TiCl_4$ solutions in 60 min can be represented by a relation of the type

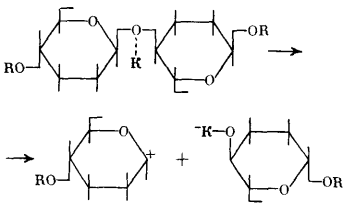
$$DP_{av} = 259.05\varepsilon - 432, \quad r = 0.995.$$

The shape of the curve relating the content of carbonyl groups in the degraded specimens to the dielectric constant, the number of carbonyl groups being determined by the Szabolcs method, makes it possible to reiterate with a greater degree of certainty the conclusion reached above: the degree of degradation of cellulose decreases monotonically with increase of ε, which is described quantitatively by the equation

$$[CO] = \frac{1.345}{\varepsilon} + 0.043, \quad r = 0.940.$$

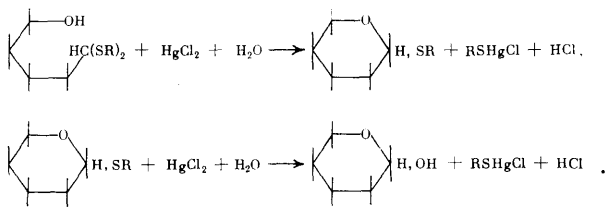
The differential molecular weight distribution curves for the specimens subjected to brief treatment with Lewis acid solutions in dry organic solvents in most cases have a shape close to that of the Gaussian distribution and indicate the formation of specimens homogeneous as regards the degree of polymerisation[139-141], in which the water-soluble fraction does not exceed 2% and there are no macromolecules with a degree of polymerisation exceeding 1000.

The mechanism of the decomposition of the cellulose chain may be represented by a scheme providing for the coordination of the Lewis acid molecule to the ring or glycosidic oxygen atoms and for subsequent heterolysis of the $C_{(1)}$–O bond with formation of a $C_{(1)}$ carbonium ion:



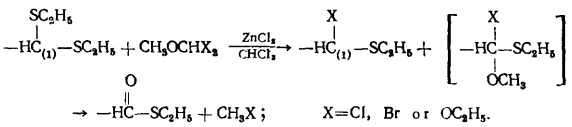
V. REACTIONS OF SUGAR THIOACETALS

The formation of thioglycosides in the decomposition of dithioacetals in the presence of mercury(II) chloride, established by Schneider and Sepp[142-144] and then by Pacsu and coworkers[145,146] is of great importance for the development of the chemistry of sugar thio-derivatives. The composition of the products of the decomposition of the dithioacetals depends on the reaction conditions and the $HgCl_2$ concentration. In the presence of an excess of $HgCl_2$, stable and readily separated complexes of the dithioacetals with $HgCl_2$, which have been proposed for the identification of sugars[147,148], are formed. The degree of decomposition of the dithioacetals depends on the ratios of the rate constants for the successive stages of the formation of the thioglycoside and its decomposition to the monosaccharide:

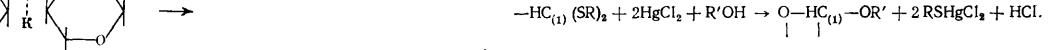


The highest yield has been observed for glucose and ribose thioacetals; the rate of the second stage for mannose and xylose thioacetals is higher than that of the first and it is in practice impossible to isolate the thioglycoside from the reaction mixture[149,150]. It is important to note that thioglycosides in the furanose form may be synthesised by this method. This is favoured by carrying out the reaction at low temperatures and by adding mercury(II) oxide in order to bind hydrogen chloride[151]. The corresponding thioglycopyranosides are produced together with the furanose forms[152].

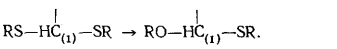
The cleavage of the monosaccharide mercaptals in the presence of catalytic amounts of $ZnCl_2$ and α-halogenoethers is accompanied by the formation of products of the substitution of one of the mercapto-groups by a halogen atom and an alkoxy-residue[59]:



In absolute alcohol in the presence of $HgCl_2$, the decomposition of dithioacetals leads to the formation of the corresponding *O*-alkyl glycoside in the furanose or pyranose form[147,151]:



At room temperature in the presence of added mercury(II) oxide, glycofuranosides are formed in high yields[149,153,154]; on the other hand, the formation of glycopyranosides is promoted by an increase of temperature and an acidic pH of the medium[155]. According to Pacsu[156], the formation of *O*-alkyl glycosides under the conditions of the alcoholysis of dithioacetals is preceded by the formation of a mixed acetal:

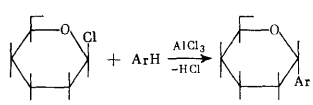


The latter is an intermediate in the *O*-glycosylation reaction. The formation of acetal forms of this kind has been confirmed experimentally[157,158].

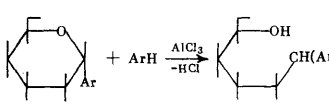
A change in the reaction conditions can lead to the formation of dialkyl acetals, as shown[159] for the diethyl dithioacetal of L-rhamnose. The highest yield of the acetal is observed on low-temperature treatment of the diethyl dithioacetal of fructose in methanol with mercury(II) chloride in the presence of an excess of mercury(II) oxide[156]. When the reaction is carried out in aqueous solution in the presence of $HgCl_2$, the thioacetal protecting groups are fully removed[160,161]. This method is used widely in carbohydrate chemistry, particularly in the synthesis of acetylated *al*-forms of monosaccharides[160] sugars with nitrogen atoms in the carbohydrate ring[162,163], and oligosaccharides[164].

VI. THE FORMATION OF CARBON–CARBON BONDS

The formation of *C*-glycosides as a result of arylation at $C_{(1)}$ of acetylglucosyl chloride in the presence of anhydrous aluminium chloride, observed by Hurd and Bonner[165,166], may serve as an analogue of the Friedel–Crafts reaction in carbohydrate chemistry:



With increase of $AlCl_3$ concentration, an acyclic disubstituted arylation product is formed:



This reaction is complicated by a number of side processes and for this reason has not found applications in the synthesis of *C*-glycosides[167].

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Summarising the data described, we may note that, although Lewis acids have found fairly extensive applications in the synthesis of various derivatives of simple sugars, nevertheless their possibilities have been by no means fully exhausted. It is already clear that the range of their activity is much wider than that of Brønsted acids, which are extensively used in carbohydrate chemistry. The interaction of Lewis acids with polysaccharides has been investigated to a much lesser extent and the studies have been concerned only with cellulose, without involving other polysaccharides. With rare exceptions, this has been basically applied research. The results which have already been obtained urgently require a further profound development of research in this field.

REFERENCES

1. N.K.Kochetkov, A.F.Bochkov, B.A.Dmitriev, A.I.Usov, O.S.Chizhov, and V.N.Shibaev, "Khimiya Uglevodov" (Chemistry of Carbohydrates), Izd. Khimiya, Moscow, 1967.
2. W.W.Pigman, "Chemistry of Carbohydrates", Acad.Press, New York, 1948.
3. V.A.Afanas'ev, "Mekhanizmy Aktivatsii Molekul Uglevodov v Usloviyakh Kislotno-Osnovnogo Kataliza" (Mechanisms of the Activation of Carbohydrate Molecules under the Conditions of Acid–Base Catalysis), Izd.Ilim, Frunze, 1971.
4. V.A.Afanas'ev, F.V.Pishchugin, N.I.Trushkina, and V.A.Kharmats, Symposium, "Gomogennyi Kataliz, Materialy I Koordinatsionnogo Soveshchaniya po Gomogennomu Katalizu" (Homogeneous Catalysis. Proceedings of the I st Coordinating Conference on Homogeneous Catalysis), Izd.Ilim, Frunze, 1970, p.41.
5. V.A.Afanas'ev, I.F.Strel'tsova, N.I.Trushkina, O.V.Dronov, and F.V.Pishchugin, "Stroenie i Reaktsionnaya Sposobnost' N-Glikozidov" (The Structure and Reactivity of *N*-Glycosides), Izd.Ilim, Frunze, 1976.
6. P.G.Ashmore, "Catalysis and Inhibition of Chemical Reactions" (Translated into Russian), Izd.Mir, Moscow, 1966.
7. H.S.Isbell and H.L.Frush, J.Org.Chem., **23**, 1309 (1958).
8. H.Simon and D.Palm, Chem.Ber., **98**, 433 (1965).
9. B.Capon and B.E.Connett, Tetrahedron Letters, 1395 (1964).
10. B.Capon, Chem.Rev., 69, 407 (1969).
11. J.N.Brønsted and E.A.Guggenheim, J.Amer. Chem.Soc., 49, 2554 (1927).
12. F.A.Long and M.A.Paul, Chem.Rev., 57, 935 (1957).
13. R.Bell, in "Kataliz. Issledovanie Gomogennykh Protsessov" (Catalysis. Studies on Homogeneous Processes) (Translated into Russian), Inostr.Lit., Moscow, 1957, p.5.
14. L.P.Hammett, "Physical Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1972.
15. F.Stockhausen and L.Gatterman, Ber., **25**, 3521 (1892).
16. H.Skraup and R.Kreman, Monatsh., **22**, 375 (1901).
17. A.Kunz and C.S.Hudson, J.Amer.Chem.Soc., **48**, 1978, 2435 (1926).
18. S.Ahrland, J.Chatt, and N.R.Davis, Quart.Rev., **12**, 265 (1958).
19. D.P.N.Satchell and R.S.Satchell, Quart.Rev., **25**, 171 (1971).
20. J.F.Deters, P.A.McCusker, and R.C.Pilger,Jnr., J.Amer.Chem.Soc., 90, 4583 (1968).
21. I.I.Moiseev, Symposium, "Problemy Kinetiki i Kataliza" (Problems in Kinetics and Catalysis), Izd. Nauka, Moscow, 1968, No.12, p.50.
22. M.E.Krasnyanskii, A.O.Litinskii, and E.I.Shifrovich, Teor.Eksper.Khim., 10, 536 (1974).
23. I.Osamu and H.Masahiro, Chem.Letters, 567 (1973).
24. Z.Csürös, Gy.Deák, and L.Fenichel, Acta.Chim. Acad.Sci.Hung., **21**, 169 (1959).
25. Z.Csürös, Gy.Deák, L.Fenichel, S.Holly, and J.Pálinkas, Acta.Chim.Acad.Sci.Hung., 56, 325 (1968).
26. Z.Csürös, Gy.Deák, I.Gyurkovics, S.Holly, M.Haraszthy-Papp, A.Török-Kalmar, and E.Zara-Kaczian, Acta.Chim.Acad.Sci.Hung., 55, 347 (1968).
27. Z.Csürös, Gy.Deák, I.Gyurkovics, M.Haraszthy-Papp, and E.Zara-Kaczian, Acta.Chim.Acad.Sci. Hung., 67, 93 (1971).
28. Y.Avny, R.Rahman, and A.Zilkha, J.Macromolec. Sci., A6, 1427 (1972).
29. B.Capon and D.Thacker, J.Chem.Soc., 1010 (1967).
30. E.Pacsu, Ber., 61, 137, 1508 (1928).
31. E.Pacsu, J.Amer.Chem.Soc., 52, 2568, 2571 (1930).
32. E.Pacsu, Methods in Carbohydrate Chem., 2, 376 (1963).
33. R.E.Reeves and L.W.Mazzeno, J.Amer.Chem. Soc., 76, 2219 (1954).
34. B.Lindberg, Acta Chem.Scand., 2, 426, 534 (1948).
35. B.Lindberg, Acta Chem.Scand., 3, 1153, 1350, 1355 (1949).
36. B.Lindberg, Acta Chem.Scand., 5, 340 (1951).
37. I.J.Goldstein and W.H.Whelen, J.Chem.Soc., 4264 (1963).
38. D.Thacker and T.L.V.UlBricht, J.Chem.Soc., 333 (1968).
39. P.M.Collins, W.G.Overend, and B.A.Rayner, Carbohyd.Res., 31, 1 (1973).
40. R.U.Lemieux and W.P.Shyluk, Canad.J.Chem., 33, 120 (1955).
41. T.D.Audichya, T.R.Ingle, and I.L.Rose, Indian J. Chem., 41, 704 (1973).
42. G.Wagner and E.Fickweiler, Arch.Pharm., 298, 62 (1965).
43. G.Schmidt and J.Farkas, Coll.Czech.Chem.Comm., 31, 4442 (1966).
44. B.N.Stepanenko, E.M.Kaz'mina, and Z.S.Dubinkina, Uspekhi Khim., 42, 1121 (1973) [Russ.Chem.Rev., No.6 (1973)].
45. B.E.Tilley, D.W.Porter, and R.W.Gracy, Carbohyd.Res., 27, 289 (1973).
46. S.Kolka and Ja.Sokolowski, Roczniki Chem., 48, 439 (1974).
47. R.U.Lemieux, in "Metody Khimii Uglevodov" (Methods of Carbohydrate Chemistry) (Translated into Russian), Izd.Mir, Moscow, 1967, p.125.
48. W.A.Bonner, J.Amer.Chem.Soc., 80, 3372 (1958).
49. E.Pacsu and F.V.Rich, J.Amer.Chem.Soc., 57, 587 (1935).

50. L.J.Haynes and F.H.Newth, Adv.Carbohyd.Chem., 10, 207 (1955).
51. W.Korytnyk and J.A.Mills, J.Chem.Soc., 636 (1959).
52. G.Zemplén and A.Gerecs, Ber., 64, 1545 (1931).
53. I.Johansson, B.Lindberg, and O.Theander, Acta Chem.Scand., 17, 2019 (1963).
54. P.L.Duretts, L.Hough, and A.C.Richardson, J. Chem.Soc., Perkin Trans.I, 97 (1974).
55. R.U.Lemieux and C.Brice, Canad.J.Chem., 30, 295 (1952).
56. R.U.Lemieux, Adv.Carbohyd.Chem., 9, 1 (1954).
57. R.U.Lemieux, Canad.J.Chem., 29, 1079 (1951).
58. R.U.Lemieux and C.Brice, Canad.J.Chem., 33, 109 (1955).
59. I.Farkas, M.Menyhart, R.Bognár, and H.Gross, Chem.Ber., 98, 1419 (1965).
60. H.Gross and I.Farkas, Chem.Ber., 93, 95 (1960).
61. H.Gross and J.Gloede, Chem.Ber., 96, 1387 (1963).
62. S.Allen, T.G.Bonner, E.J.Bourne, and N.M.Saville, Chem.Ind.(London), 630 (1958).
63. T.G.Bonner, E.J.Bourne, and S.McNally, J. Chem.Soc., 2929 (1960).
64. T.G.Bonner and N.M.Saville, J.Chem.Soc., 2851 (1960).
65. L.Hough and R.S.Theobald, in "Metody Khimii Uglevodov" (Methods of Carbohydrate Chemistry) (Translated into Russian), Izd.Mir, Moscow, 1967, p.110.
66. T.G.Bonner and E.J.Bourne, in "Metody Khimii Uglevodov" (Methods of Carbohydrate Chemistry) (Translated into Russian), Izd.Mir, Moscow, 1967, p.113.
67. B.Pettersson and O.Theander, Acta Chem.Scand., B-28, 29 (1974).
68. F.R.Seymour, Carbohyd.Res., 30, 327 (1973).
69. G.J.F.Chittenden, Carbohyd.Res., 31, 127 (1973).
70. A.F.Pavlenko, N.I.Belogortseva, A.I.Kalinovskii, and Yu.S.Ovodov, Izv.Akad.Nauk SSSR, Ser.Khim., 1593 (1974).
71. I.O.Mastronardi, S.M.Flematti, J.O.Deferrari, and E.G.Gros, Carbohyd.Res., 3, 177 (1966).
72. E.G.Gros and E.M.Gruneiro, Carbohyd.Res., 23, 148 (1972).
73. A.N.de Belder, Adv.Carbohyd.Chem., 20, 220 (1965).
74. H.T.Fletcher, in "Metody Khimii Uglevodov" (Methods of Carbohydrate Chemistry) (Translated into Russian), Izd.Mir, Moscow, 1967, p.161.
75. O.T.Schmidt, in "Metody Khimii Uglevodov" (Methods of Carbohydrate Chemistry) (Translated into Russian), Izd.Mir, Moscow, 1967, p.162.
76. A.L.Raymond and E.F.Schroeder, J.Amer.Chem. Soc., 70, 2785 (1948).
77. W.L.Glen, G.S.Myers, and G.A.Grant, J.Chem. Soc., 2568 (1951).
78. H.B.Wood, H.W.Diehe, and H.G.Fletcher, J. Amer.Chem.Soc., 79, 1986 (1957).
79. R.W.Jeanlos and D.A.Jeanlos, J.Amer.Chem.Soc., 79, 2579 (1957).
80. S.H.Dorcheus and D.G.Williams, J.Org.Chem., 28, 775 (1963).
81. J.Pacák and M.Černy, Coll.Czech.Chem.Comm., 28, 541 (1963).
82. K.L.Matta, E.A.Z.Johnson, and J.J.Barlow, Carbohyd.Res., 32, 396 (1974).
83. J.G.Buchanan and R.M.Saunders, J.Chem.Soc., 1796 (1964).
84. B.Coxon and H.G.Fletcher Jnr., J.Org.Chem., 26, 2892 (1961).
85. C.S.Hudson and D.H.Brauns, J.Amer.Chem.Soc., 37, 2736 (1915).
86. F.B.Cramer and E.Pacsu, J.Amer.Chem.Soc., 59, 1148 (1937).
87. R.Barker, J.Org.Chem., 25, 1670 (1960).
88. Z.A.Rogovin, "Khimiya Tsellyulozy" (The Chemistry of Cellulose), Izd.Khimiya, Moscow, 1972, p.316.
89. K.S.Tsou and A.M.Seligman, J.Amer.Chem.Soc., 74, 5605 (1952).
90. C.S.Hudson and J.M.Johnson, J.Amer.Chem.Soc., 37, 1276 (1915).
91. C.S.Hudson and H.O.Parker, J.Amer.Chem.Soc., 37, 1589 (1915).
92. F.Micheel, H.Runkopf, and F.Suckfüll, Ber., 68, 1523 (1935).
93. F.Micheel and H.Runkopf, J.Amer.Chem.Soc., 70, 850 (1937).
94. F.Micheel and R.Böhm, Chem.Ber., 98, 1655, 1659 (1965).
95. J.C.Goodwin and J.E.Hodge, Carbohyd.Res., 28, 213 (1973).
96. R.L.Whistler and L.W.Donner, Carbohyd.Res., 15, 391 (1970).
97. M.E.Hill, J.Amer.Chem.Soc., 75, 3020 (1953); 76, 2329 (1954).
98. J.B.McKelvey, R.R.Benerito, and R.J.Berni, J.Appl.Polym.Sci., 9, 191 (1965).
99. E.F.Sharkova, A.D.Virnik, and Z.A.Rogovin, Vysokomol.Soed., 8, 1450 (1966).
100. A.Zemaitaitis and I.Zdanavicius, Symposium, "Khimiya i Tekhnologiya Proizvodnykh Tsellyulozy" (The Chemistry and Technology of Cellulose Derivatives), Vladimir, 1971, p.253.
101. A.D.Predvoditelev and M.S.Baksheeva, Zhur. Prikl.Khim., 45, 857 (1972).
102. F.Schmidt, Angew.Chem., 64, 536 (1952).
103. A.I.Polyakov and V.V.Smagin, Vysokomol.Soed., 14A, 1278 (1972).
104. A.I.Polyakov, L.A.Polyakova, and N.A.Lapina, USSR P.362 845 (1970); Byul.Izobret., No.3 (1973).
105. R.I.Sarybaeva, L.S.Shchelokhova, and V.A.Afanas'ev, "I Vsesoyuznaya Konferentsiya po Khimii i Fizike Tsellyulozy" (The Ist All-Union Conference on the Chemistry and Physics of Cellulose), Vol.1, "Khimiya" (Chemistry), Izd.Zinatne, Riga, 1975, p.125.
106. R.I.Sarybaeva and L.S.Shchelokhova, USSR P. 523109 (1975); Byul.Izobret., No.28 (1976).
107. G.P.Ellis and J.Honeyman, Adv.Carbohyd.Chem., 10, 95 (1955).
108. M.L.Wolfrom and A.Thompson, J.Amer.Chem. Soc., 56, 880, 1804 (1934).
109. C.D.Hurd and W.A.Bonner, J.Org.Chem., 11, 50 (1946).
110. J.Conchie, G.A.Levvy, and C.A.Marsh, Adv. Carbohyd.Chem., 12, 157 (1957).
111. R.J.Ferrier, R.W.Hay, and N.A.Vethaviyasar, Carbohyd.Res., 27, 55 (1973).
112. E.Lukevics, A.E.Zablotskaya, and N.I.Solomennikova, Uspekhi Khim., 43, 370 (1974) [Russ.Chem. Rev., No.2 (1974)].
113. B.Helferich and K.Weiss, Chem.Ber., 89, 314 (1956).
114. B.Helferich and J.Zirner, Chem.Ber., 95, 2604 (1962).

115. P.W.Kent, Research (London), 3, 427 (1950).
116. B.Helferich, A.Doppstadt, and G.A.Gottschlich, Naturwiss., 40, 441 (1953).
117. R.Kuhn and W.Kirschenlohr, Chem.Ber., 86, 1331 (1953).
118. N.K.Kochetkov, A.Khorlin, and A.F.Bochkov, Tetrahedron Letters, 289 (1964).
119. N.K.Kochetkov, A.Khorlin, and A.F.Bochkov, Tetrahedron, 23, 693 (1967).
120. N.K.Kochetkov, A.Ya.Khorlin, and A.F.Bochkov, Dokl.Akad.Nauk SSSR, 162, 104 (1965).
121. N.K.Kochetkov, A.Ya.Khorlin, and A.F.Bochkov, Zhur.Obshch.Khim., 37, 338 (1967).
122. N.K.Kochetkov, A.Ya.Khorlin, A.F.Bochkov, L.B.Demushkina, and I.O.Zolotukhin, Zhur. Obshch.Khim., 37, 1272 (1967).
123. A.F.Bochkov and Ya.V.Voznyi, Carbohyd.Res., 32, 1 (1974).
124. A.F.Bochkov and V.M.Kalinevitch, Carbohyd.Res., 32, 9 (1974).
125. A.Ya.Khorlin, A.F.Bochkov, and N.K.Kochetkov, "Khimiya i Obmen Uglevodov, Materialy III Vsesoyuznoi Konferentsii po Probleme 'Khimiya i Obmen Uglevodov'" (The Chemistry and Metabolism of Carbohydrates. Proceedings of the IIIrd All-Union Conference on the Problem of the 'Chemistry and Metabolism of Carbohydrates'), Izd.Nauka, Moscow, 1965, p.58.
126. N.K.Kochetkov, A.Ya.Khorlin, A.F.Bochkov, and I.G.Yazlovetskii, Carbohyd.Res., 1, 84 (1966).
127. N.K.Kochetkov, A.F.Bochkov, and I.G.Yazlovetskii, Izv.Akad.Nauk SSSR, Ser.Khim., 1872 (1966).
128. N.K.Kochetkov, A.F.Bochkov, I.G.Yazlovetskii, and V.I.Snyatkova, Izv.Akad.Nauk SSSR, Ser.Khim., 1802, 1812, 1818 (1968).
129. Yu.L.Pogosov and Z.A.Rogovin, Uspekhi Khim., 30, 1215 (1961) [Russ.Chem.Rev., No.10 (1961)].
130. V.V.Korshak, O.P.Golova, V.A.Sergeev, and N.M.Merlis, Vysokomol.Soed., 3, 477 (1961).
131. F.Micheel, O.-E.Brodde, and K.Reinkihg, Annalen, 127 (1974).
132. W.H.Lindenberger and C.Schuerch, J.Polymer Sci., 11, 1225 (1973).
133. E.O'Brien, E.E.Lee, P.S.O'Colla, and U.Egan, Carbohyd.Res., 32, 31 (1974).
134. N.K.Kochetkov, E.M.Klimov, and B.M.Kislov, Izv.Akad.Nauk SSSR, Ser.Khim., 2900 (1973).
135. R.I.Sarybaeva, Candidate's Thesis, Institute of General Chemistry, Academy of Sciences of Kirghiz SSR, Frunze, 1969.
136. V.I.Ivanov, V.A.Afanas'ev, and R.I.Sarybaeva, Dokl.Akad.Nauk SSSR, 192, 1043 (1970).
137. T.V.Vasil'kova, R.I.Sarybaeva, and A.S.Suntankulova, "Materialy XX Nauchno-Tekhnicheskoi Konferentsii Frunzenskogo Politekhnicheskogo Instituta, Frunze, Iyun', 1974" (Proceedings of the XXth Scientific and Technical Conference of the Frunze Polytechnic Institute, Frunze, June, 1974) (in the Press).
138. R.I.Sarybaeva, T.V.Vasil'kova, A.S.Sultankulova, M.S.Kozhanova, and V.A.Afanas'eva, "I Vsesoyuznaya Konferentsiya po Khimii i Fizike Tsellyulozy" (The Ist All-Union Conference on the Chemistry and Physics of Cellulose), Vol.1, "Khimiya" (Chemistry), Izd.Zinatne, Riga, 1975, p.116.
139. R.I.Sarybaeva, V.A.Afanas'ev, V.I.Ivanov, and N.T.Yatsenko, Izv.Akad.Nauk Kirgiz.SSR, No.5, 61 (1972).
140. R.I.Sarybaeva, N.T.Yatsenko, and V.I.Ivanov, Symposium, "Perspektivy Ispol'zovaniya Prirodnykh Resursov Kirgizii dlya Razvitiya Khimicheskikh Proizvodstv" (Prospects for the Utilisation of the Natural Resources of Kirghizia for the Development of Chemical Industries), Izd.Ilim, Frunze, 1973, p.70.
141. R.I.Sarybaeva, T.V.Vasil'kova, and A.S.Sultankulova, Vysokomol.Soed., 27 (B), 541 (1975).
142. W.Schneider and J.Sepp, Ber., 49, 2054 (1916).
143. W.Schneider, J.Sepp, and O.Stiehler, Ber., 51, 220 (1918).
144. W.Schneider, R.Gille, and K.Eisfeld, Ber., 61, 1205 (1937).
145. J.W.Green and E.Pacsu, J.Amer.Chem.Soc., 59, 1205 (1937).
146. E.Pacsu, in "Metody Khimii Uglevodov" (Methods of Carbohydrate Chemistry) (Translated into Russian), Izd.Mir, Moscow, 1967, p.184.
147. E.Hardegger, E.Schreier, and Z.el Heweihi, Helv. Chim.Acta, 33, 1159 (1950).
148. Z.el Heweihi, Chem.Ber., 86, 781, 862 (1953).
149. H.Zinner, A.Koine, and H.Nimz, Chem.Ber., 93, 2705 (1960).
150. M.L.Wolfrom, Z.Yosizawa, and B.O.Juliano, J.Org.Chem., 24, 1529 (1959).
151. E.Pacsu and J.W.Green, J.Amer.Chem.Soc., 58, 1823 (1936).
152. M.L.Wolfrom and Z.Yosizawa, J.Amer.Chem. Soc., 81, 3474 (1959).
153. J.W.Green and E.Pacsu, J.Amer.Chem.Soc., 60, 2056 (1938).
154. M.L.Wolfrom, P.McWain, R.Pagnucco, and A.Thompson, J.Org.Chem., 29, 454 (1964).
155. E.Pacsu and N.Ticharich, Ber., 3008 (1939).
156. E.Pacsu, J.Amer.Chem.Soc., 60, 2277 (1938); 61, 1671 (1939).
157. M.L.Wolfrom and D.I.Weisblat, J.Amer.Chem. Soc., 62, 878 (1940).
158. M.L.Wolfrom, D.I.Weisblat, and A.R.Hanze, J. Amer.Chem.Soc., 62, 3246 (1940); 66, 2065 (1944).
159. J.W.Green and E.Pacsu, J.Amer.Chem.Soc., 60, 2288 (1938).
160. M.L.Wolfrom, J.Amer.Chem.Soc., 51, 2188 (1929); 52, 2464 (1930).
161. M.L.Wolfrom and S.W.Weisbrot, J.Amer.Chem. Soc., 60, 854 (1938).
162. T.H.Haskell and S.Hanessian, J.Org.Chem., 28, 2604 (1963).
163. S.Hanessian, Carbohyd.Res., 1, 178 (1965).
164. P.A.J.Gorin, Canad.J.Chem., 40, 275 (1962).
165. C.D.Hurd and W.A.Bonner, J.Amer.Chem.Soc., 67, 1664, 1759, 1977 (1945).
166. W.A.Bonner, Adv.Carbohyd.Chem., 6, 251 (1951).
167. Yu.A.Zhdanov, Uspekhi Khim., 25, 1165 (1956).

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