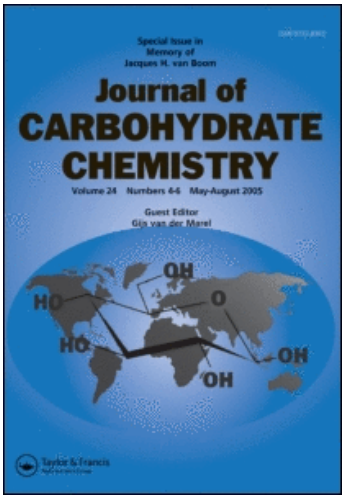

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Zinc-*N*-Base Mediated Synthesis of Pyranoid Glycals Mechanistic Studies

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ZINC–*N*-BASE MEDIATED SYNTHESIS OF PYRANOID GLYCALS

MECHANISTIC STUDIES

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ABSTRACT

Reactions of acetobromoglucose **1** or acetylated 1-bromo-D-galactopyranosyl cyanide **3** with zinc dust in the presence of a *N*-base (1-methylimidazole, 4-methylpyridine, or triethylamine, pyridine, respectively) in ethyl acetate or benzene were efficiently inhibited by 10-30 mol % of 1,4-dinitrobenzene, elemental sulfur, or carbon tetrachloride. Presence of glycosyl radicals in these reactions was also shown by trapping them with *tert*-dodecyl mercaptan or methyl acrylate. Based on these observations and the high yielding formation of glycal derivatives **2** and **4** of high purity a free radical chain mechanism is proposed for the transformations.

INTRODUCTION

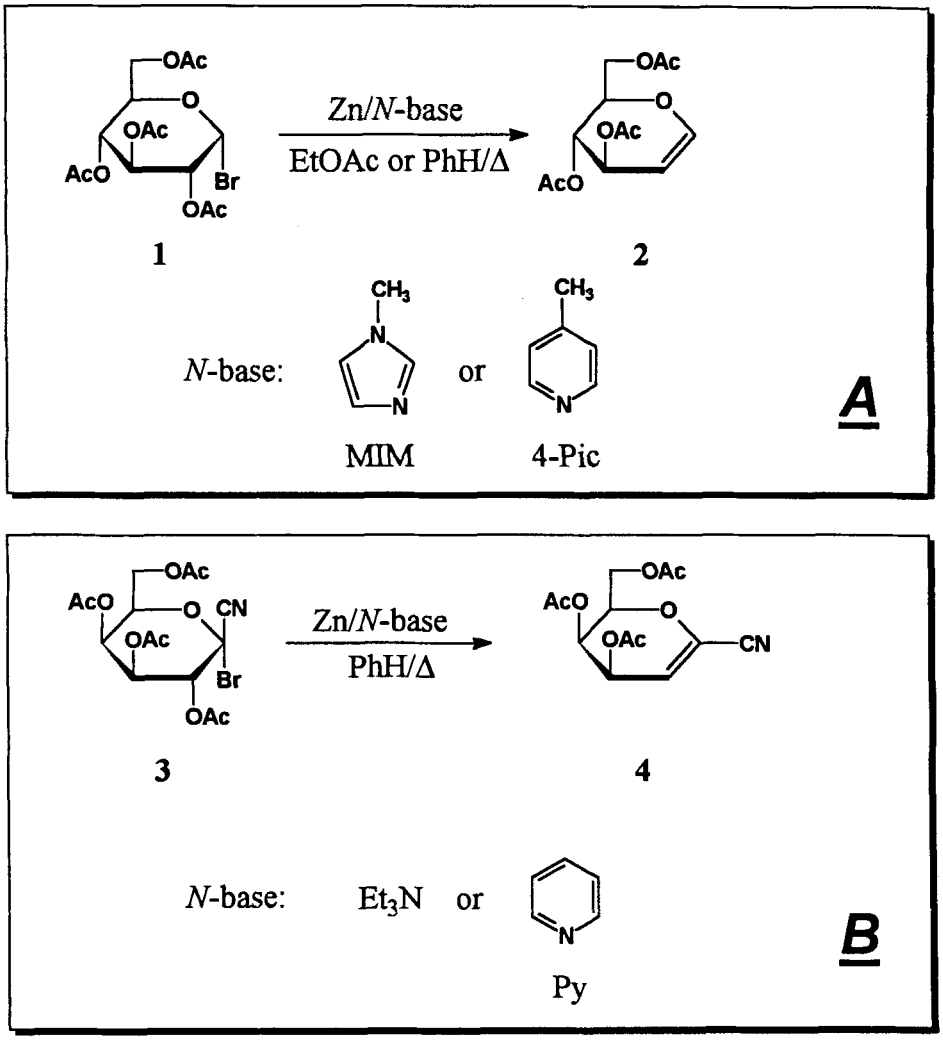
Glycals are one of the most frequently used carbohydrate building blocks[1] in carbohydrate and natural product syntheses. Although this class of compounds has been known for almost a century[2] newer and newer methods of preparation appear continually.[3]

A few years ago one of us published a simple, large scale, adaptable procedure in which Zn-dust in aprotic solvents (benzene, ethyl acetate, tetrahydrofuran, acetone, dichloromethane) in the presence of a heterocyclic *N*-base (4-methylpyridine, 1-methylimidazole) was used for the preparation of acylated pyranoid glycals[4] from the corresponding glycosyl bromides. This method was applied also for the synthesis of glycal derivatives with a carbon substituent attached to C-1,[5] and was found to be useful in other syntheses as well.[6]

Mechanistic investigations on the glycal forming reaction under the classical Fischer-Zach conditions accounting for the appearance of solvolysis products and anhydro alditols were surveyed.[7] That general picture was refined on the basis of careful analysis of the reaction mixtures by capillary gas chromatography (CGC)[8] corroborating the role of glycosylium ions on the reaction pathway. The occurrence of such by-products as 2-deoxy- and 2,3-unsaturated pyranose derivatives was attributed to a fast rearrangement of the glycosylium ion via a 1,2-dioxolenium ion[9] to the C-2 carbocation followed by a two-electron reduction and subsequent protonation or β-elimination. Under conditions of the zinc–*N*-base mediated glycal synthesis, formation of a glycosylium ion is highly improbable because the applied aprotic and apolar solvents disfavour[10] ionization and dissociation of the starting glycosyl halide. Because of our interest in the mechanism of glycal formation[8] and the usefulness of the method[4-6] we have explored the nature of the reactive intermediates appearing in this reaction and propose a probable mechanism for the transformation.

RESULTS AND DISCUSSION

As models, reactions **A**[4] and **B**[5a,b] were chosen and carried out in the presence of various additives. The composition of the reaction mixtures **A** was determined by CGC (Table 1). The presence of one equivalent of 1-methylimidazole (MIM) or another *N*-base was an absolute necessity for the reaction since with zero or less than 1 equivalent the ratio of the glucal sharply decreased (*Entries 1-3* and *12-14*). A small amount of 1,4-dinitrobenzene (*p*DNB) used for trapping radical-anions[11] hindered the formation of glucal (*Entries 4* and *15*) as did the radical traps[12] carbon-tetrachloride



(CCl_4) (*Entries 5* and *16*) and elemental sulfur (S_8) (*Entries 7* and *17*). In the latter case the main component of the crude reaction mixtures was identical with the starting material **1** as judged by TLC and ^1H NMR. With an excess of methyl acrylate the known C-glucosyl derivative **10**[13] obtainable by addition of the nucleophilic glucosyl radical to the electron deficient double bond appeared in remarkable amount (*Entry 8*). In the presence of *tert*-dodecyl mercaptan (*t*-DoSH) (*Entry 18*), an efficient hydrogen donor[14] the acetylated anhydro glucitol **6** was the main by-product. Addition of large amounts of alcohols (*Entries 9* and *10*) was only slightly detrimental for the glucal formation similarly

TABLE 1. Composition[a] of the reaction mixtures *A* in the presence of additives

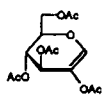
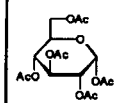
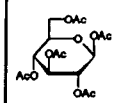
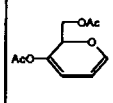
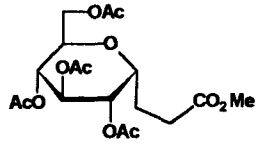
Entry	MIM (eq)	Additive (eq)	Reaction time (h)	2 (%) 	5 (%) 	6 (%) 	7 (%) 	8 (%) 	9 (%) 	Unknown and/or others (%)
EtOAc										
1.	1	--	3	98	--	--	--	2	--	--
2.	--	--	3	15	--	--	20	22	16	27
3.	0.25	--	2.5	41	--	--	14	22	6	17
4.	1	0.1 *p*DNB[d]	4	42	10	--	11	37	--	--
5.	1	0.06 CCl_4	1.5	62	--	--	12	19	2	5
6.	--	0.25 CCl_4	1	1	8	--	27	33	--	31
7.[b]	1	0.3 S_8	5	--	1	--	14	80	--	5
8.[c]	1	22 Me-acrylate		71	--	--	--	--	--	29 **10**
9.	1	50 MeOH	3	88	2	--	--	--	1	2 **7** **11**
10.	1	32 *i*PrOH	1	91	--	1	1		3	4
11.	1	5 Bu_4NHSO_4	0.5	79	1	--	2	10	--	8

TABLE 1. *continued*

PhH										
12.	1	--	3.5	90	1	--	--	9	--	--
13.	--	--	1.5	2	--	--	21	44	--	33
14.	0.25	--	2	1	--	--	10	87	1	1
15.	1	0.3 *p*DNB[d]	5	11	5	--	7	75	--	2
16.	1	0.25 CCl_4	3	2	--	--	46	51	--	1
17.[b]	1	0.1 S_8	3	5	40	--	8	26	--	21
18.[c]	1 4-Pic	4 *t*-DoSH		75	--	25	--	--	--	--
19.	1	1 PhCHO	0.5	93	--	2	1	1	--	3

a. By capillary gas chromatography of the worked up mixtures after exhaustive acetylation (see Experimental).
b. ^{1}H NMR spectrum of the worked up mixture showed acetobromoglucose **1** to be present at least 90 %.
c. On the basis of the ^{1}H NMR spectrum.
d. 1,4-dinitrobenzene.



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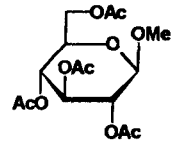

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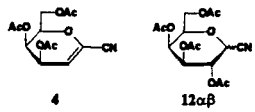
to the effect of hydrogensulfate ions (*Entry 11*). Benzaldehyde caused no severe change in the course of the reaction (*Entry 19*).

The effects of additives in transformation **B** are collected in Table 2. Without *N*-base no reaction took place (*Entry I*). With 1 equivalent of a *N*-base the transformation was complete in very short periods (*Entries II, VI, XIII*) to give **4** of very high purity. In the presence of inhibitors (*Entries IV, V, VII-XI*) the reaction times significantly increased or nothing happened at all. Application of a large excess of triethylamine (Et_3N) (*Entry III*) resulted in the formation of anomeric galactopyranosyl cyanides (**12**αβ) besides **4** similarly to that effected by *t*-DoSH (*Entry XII*).

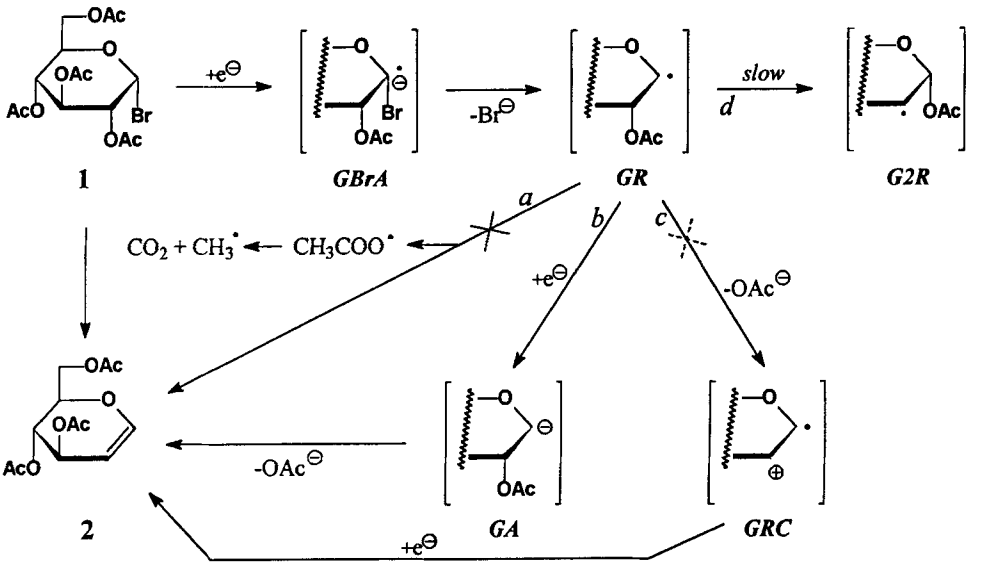
These experimental findings allow one to conclude that under the given conditions, radical-anions of the glucosyl bromide (***GBrA***) and glucosyl radicals (***GR***) appear on the reaction pathway (Scheme 1). ***GBrA*** can be formed by a single electron transfer (SET) from the zinc and can then lose a bromide ion to give ***GR***. Further transformation of ***GR*** may follow several routes. According to *route a* loss of an acetyl radical would lead directly to the product **2**. Although this process is enthalpically disfavoured,[15] it was more thoroughly examined because during photolysis of glucosylcobaloximes used for generation of ***GR*** formation of glucal **2** in 45 % yield was reported.[16] As acyloxyl radicals ($RCO_2^{\cdot}$) are known to fragment into carbon dioxide (CO_2) and the corresponding radical ($R^{\cdot}$) at very high rates,[17] formation of CO_2 was investigated. No traces of CO_2 could be detected, and because of this and the enthalpic considerations, *route a* is thought to be highly improbable.

Another possibility for ***GR*** to be transformed into **2** is to take up an electron and to lose an acetate ion. These events may occur in different sequences as shown by *routes b* and *c*. It would be straightforward to consider *route b* to be the main pathway in analogy with the mechanism of glycal formation under Fischer-Zach conditions.[7,8] However, the experimental findings show no direct evidence (except the formation of glucal itself[18]) for the presence of the corresponding glucosyl anion (***GA***) since on addition of proton scources (*Entries 9-11*) the anhydroglucitol **6** does not appear. The very small proportion of **6** in the presence of 2-propanol (*Entry 10*) may be due to hydrogen transfer to ***GR*** rather than protonation of ***GA*** because pK_a values[19] for MeOH (16) and *i*PrOH (16.5) are practically the same but the latter is a much better hydrogen donor.[14] Also with

TABLE 2. Effects of additives in reactions *B*

Entry	*N*-base (eq)	Additive (eq)	Reaction time and other observations	Product ratio[g]  4 12αβ
I.	--	--	no reaction	
II.	1 Et_3N	--	~ 15 min	95 : traces
III.	30 Et_3N	--	~ 15 min	67 : 33
IV.	1 Et_3N	0.1 *p*DNB[a]	no change during 10 hours[f]	
V.	1 Et_3N	0.1 S_8	~ 6 h no change during the first 2 hours[f]	
VI.	1 Py	--	~ 5 min	>95 : traces
VII.	1 Py	0.1 *p*DNB[a]	no change during 10 hours[f]	
VIII.	1 Py	0.1 S_8	~ 5 h no change during the first hour[f]	
IX.	1 Py	0.1 DPPH[b]	no change during 12 hours[f]	
X.	1 Py	0.1 DTBN[c]	~ 15 min	
XI.	1 Py	1 DTBN[c]	no change during 10 hours[f]	
XII.	1 Py	4 *t*-DoSH[d]	~ 15 min	64 : 36
XIII.	1 Lu[e]	--	~ 20 min	85 : 15
XIV.	--	10 1,4-dioxane	~ 1 h	

a. 1,4-dinitrobenzene
b. *N,N*-diphenyl-picryl-hydrazyl
c. di-*tert*-butylnitroxyl
d. *tert*-dodecyl mercaptan
e. 2,6-dimethylpyridine
f. The unchanged starting material was detectable by TLC.
g. Determined by ^1H NMR spectra of the worked up reaction mixtures.



Scheme 1

benzaldehyde (*Entry 19*) a *C*-electrophile, no coupling with ***GA*** was observed. The appearance of **6** in this case reflects the very good hydrogen donor ability of aldehydes.[14]

Very recently, formation of glucal **2** under electrochemical conditions was suggested[20] to follow *route c*. Similar fragmentations of α-alkoxy-β-acyloxyalkyl radicals were observed in acidic aqueous solutions,[21] where the polarity of the solvent as well as catalysis by protons may synergetically assist the cleavage of acetate ions. Since in our investigations apolar and aprotic conditions were applied which would disfavour acetate loss from ***GR*** to give a glucosyl radical cation (***GRC***) we propose *route c* to be subordinate as compared to *route b*.

The failure of the experiments to trap ***GA***, which must be an intermediate on *route b*, can be understood by assuming a very fast elimination of an acetate ion from ***GA*** to give **2**. This is corroborated by the finding that during electrolysis of **1** in acetonitrile even in the presence of acetic acid no traces of **6** could be detected, glucal **2** being the sole product.[22]

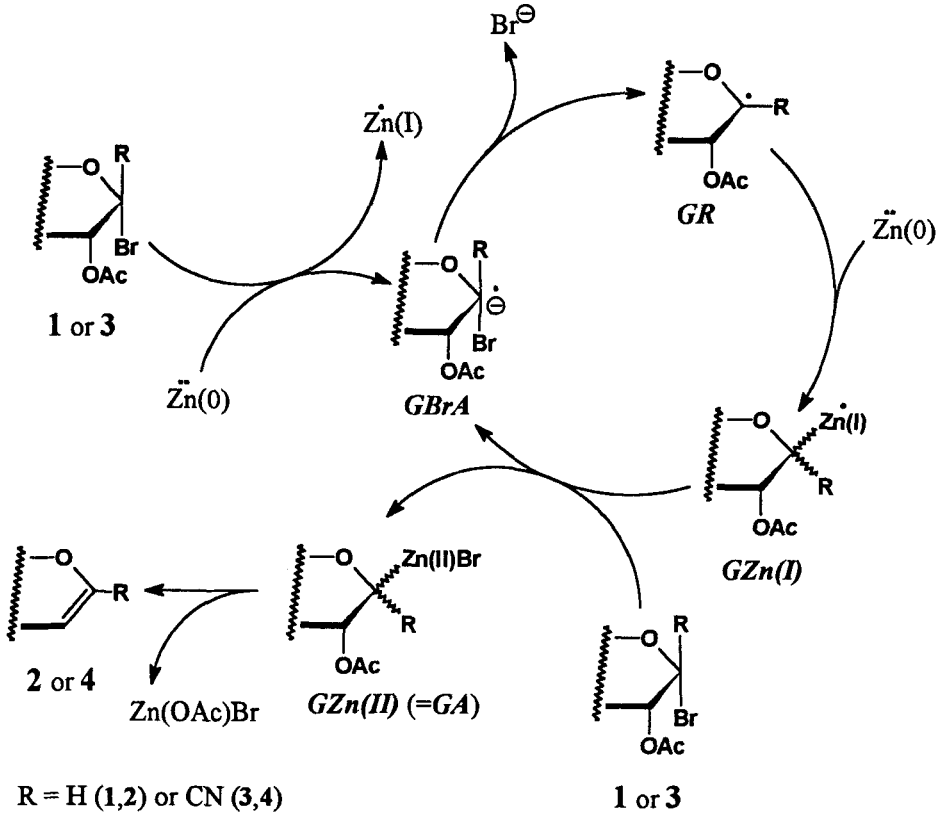
The formation of glycals through intermediates ***GBrA***, ***GR***, and ***GA*** under aprotic conditions and in the absence of efficient hydrogen donors leaves no way for the

appearance of by-products. The only possibility would be the known rearrangement[23a] of ***GR*** to the 2-deoxyglucosyl radical (***G2R***) following *route d*. However, this process is rather slow[23b] and thus cannot compete with further reduction of ***GR*** on *route b*. These peculiarities are well reflected in the generally very good yields and high purities of the products obtained under these reaction conditions.

For complete inhibition of reactions taking place according to the preferred *route b* in Scheme 1, at least one equivalent of an inhibitor should be present. It was found, however, that the applied radical-anion- and radical traps were effective in 10-30 mol% concentrations (Tables 1 and 2). Reaction **B** was completely inhibited in most cases. In reaction **A** the efficiency of inhibitors was mainly exhibited by suppressing the glucal formation and forcing the reaction to follow other pathways: e.g., elimination of hydrogen bromide from **1** to give **5**; pyrolytic de-*O*-acetylations, acetic acid eliminations and reactions of **1** with byproducts of these processes to give **7** and **8** after reacetylation; other not investigated routes leading to unidentified products (Table 1). Appearance of **9**[24] was due to further transformation of **2** mediated by Zn(II) salts formed in the reaction as it was shown by an independent experiment.[28]

These observations on the efficiency of inhibitors in much less than stoichiometric amounts parallel recent findings on the role of inhibitors in the formation of Grignard compounds and suggest a chain mechanism analogous to that proposed for that case.[25] Thus, the reaction (Scheme 2) can be started by a SET from Zn(0) to **1** or **3** to give the ***GBrA*** intermediate which can then lose a bromide ion resulting in ***GR***. Radical ***GR*** can then be further reduced by Zn(0) to give the electron rich intermediate ***GZn(I)*** or may combine with Zn(I) to give ***GZn(II)***, an equivalent of ***GA*** in a nonchain process. SET from ***GZn(I)*** to **1** or **3** to give ***GBrA*** builds up the cycle for the chain while the organozinc intermediate of anionic character (***GZn(II)***) produces **2** or **4** by losing acetate.

It is interesting to point out that these reactions show some solvent dependence. Namely, the absence of MIM in the reaction carried out in EtOAc causes less severe decrease of the glucal formation than in benzene (*Entries 1-3* and *12-14*). It was also observed several times that reaction of **3** with activated zinc[4] and MIM in EtOAc was not controllable and after some minutes of heating and stirring the mixture ran out of the top of the reflux condenser. This was never experienced when working in benzene. As can be deduced by comparing *Entries 2, 6,* and *13* the free radical chain reaction can take place



Scheme 2

to some extent in EtOAc but much less so in benzene. The observations with **3** are in keeping with the probably greater ease of formation of ***GR*** (Scheme 2) when R = CN because ***GR*** is a captodatively stabilized radical[26] in this case. The higher tendency for the chain process to take place in EtOAc might be due to a more efficient solvation of one (or more) of the intermediates in EtOAc. Most probably more favourable stabilization by coordination of solvent molecules (EtOAc rather than benzene) to the organozinc intermediate ***GZn(II)*** may occur. Also the role of the *N*-base in these reactions must be coordinative stabilization of an intermediate since it was shown that quaternary *N*-glycosyl-ammonium salts do not give glycals under the applied conditions.[4] This is confirmed by the observation that with the hindered 2,6-dimethylpyridine in reaction ***A*** no glucal was formed[4] and in reaction ***B*** the necessary reaction time increased approximately

by a factor of four (Table 2, *Entries VI* and *XIII*). Also the fact that in the presence of 1,4-dioxane a significant enhancement of the reaction time was observed (Table 2, *Entry XIV*) can be explained by the worse coordinative stabilization of the organozinc intermediate by the oxygen heterocycle as compared to the *N*-bases.[27]

EXPERIMENTAL

General methods. ^{1}H NMR spectra were recorded with a Bruker 200 WP SY (200 MHz) spectrometer for $CDCl_3$ solutions with TMS as internal standard. CGC analyses were performed with a Carlo Erba Vega 6180 gas chromatograph (DB 23 fused silica column 60 m x 0.258 mm i. d.) equipped with a cold-column injector and a flame ionization detector. Carrier gas: H_2 (flow-rate 2 mL/min). Temperature program: 140-160 °C at 5 °C/min, 160-200 °C at 6 °C/min, 200-240 °C at 8 °C/min with a final hold at 240 °C for 10 min. The components were identified by coinjection with standards.

Reaction *A* was performed on 0.5-1 mmol scales with a slight modification of the procedure described previously:[4] activated zinc dust, MIM, and an additive indicated in Table 1 were stirred at room temperature in the given solvent in the presence of 3A molecular sieves for 0.5 hour. The mixture was then heated to reflux temperature of the solvent, **1** was added in one portion, and heating and stirring were continued for the time given in Table 1. Work-up was effected as described and the product mixtures were investigated by ^{1}H NMR and, after exhaustive *O*-acetylation, by CGC.

Preparation of samples for CGC analysis. Aliquots of 80-100 mg of each solvent free crude mixture were dissolved in 2 mL $CHCl_3$, and then 20 μL of this solution together with 100 μL of a standard solution (300 mg of per-*O*-acetyl-pentaerythritol dissolved in 25 mL ethanol) were placed in Reactivials, and solvents were removed under a nitrogen stream. The residue was acetylated with 200 μL of freshly distilled acetic anhydride and ~5 mg NaOAc for 1 h at 100 °C. Acetic anhydride was then removed under reduced pressure and the residue was dissolved in 200 μL of $CHCl_3$. Finally, 0.6 μL of this solution was injected into the gas chromatograph.

Reaction *B* was performed on 0.5-1 mmol scales as described earlier[5b] in the presence of additives given in Table 2. The worked-up reaction mixtures were investigated by ^{1}H NMR where appropriate.

Detection of CO_2. Reaction ***A*** or ***B*** were each performed on a 2 mmol scale in the usual manner by purging the reaction vessel by dry N_2. The outflowing gas was led through a glass tube filled up with soda asbestos (Merck) used for CO_2 determination in elementary analysis. According to *route a* on Scheme 1 evolution of 88 mg of CO_2 should have been expected; however, no mass enhancement of the detector tube could be measured.

ACKNOWLEDGEMENT

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