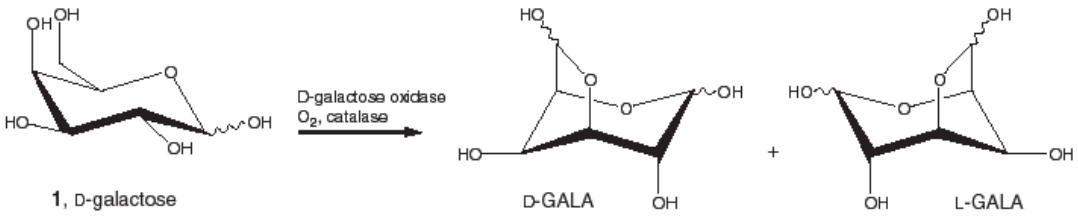
Topics in catalysis Vol. 27. Nos. 1-4, February 2004

Catalytic Conversion of Renewables

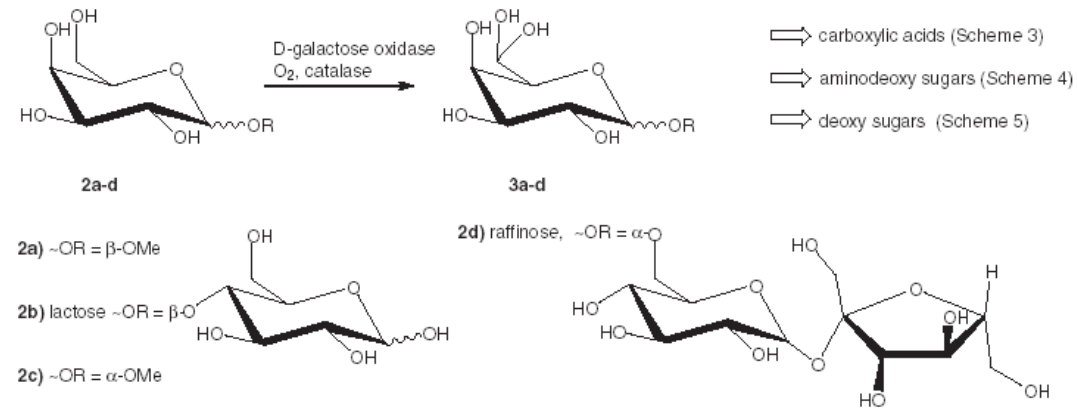
Application of galactose oxidase in chemoenzymatic one-spot cascade reactions without intermediate recovery steps

R. Schoevaart and T. Kieboom

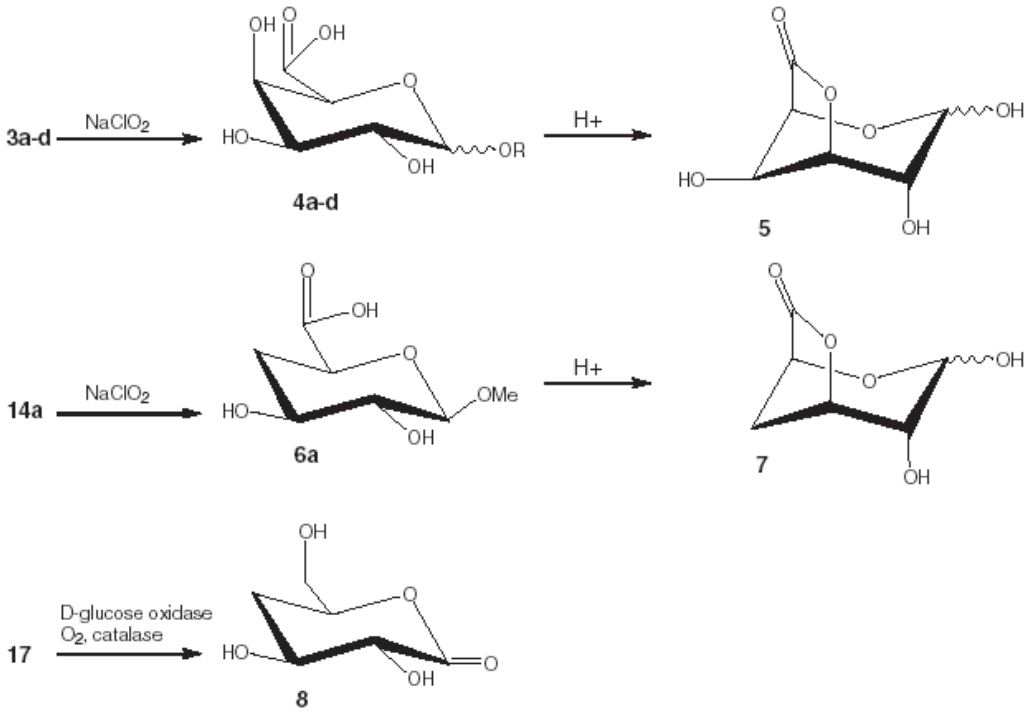
Various cascade routes starting from D-galactose derivates-via 6-CH2OH oxidation catalyzed by galactose oxidase-are reported as one-pot procedures. The approach consists of combined bio- and chemocatalytic reactions as well as "spontaneous" chemical conversions. Workup is avoided by using compatible aqueous reaction conditions for all the consecutive reactions involved. A great benefit of this method is that D-galactose containing ᵒ냐-, tri- and oligosaccharides can be modified without the use of protecting groups and without any isolation and/or purification of intermediate products in these synthesis. The one-pot cascades, consisting of up to five consecutive transformations, gave rapid access to more than 40 uronic acid, amino sugar and deoxy sugar derivatives through enzymatic, homogeneous and heterogeneous catalytic conversions in water under midl conditions.



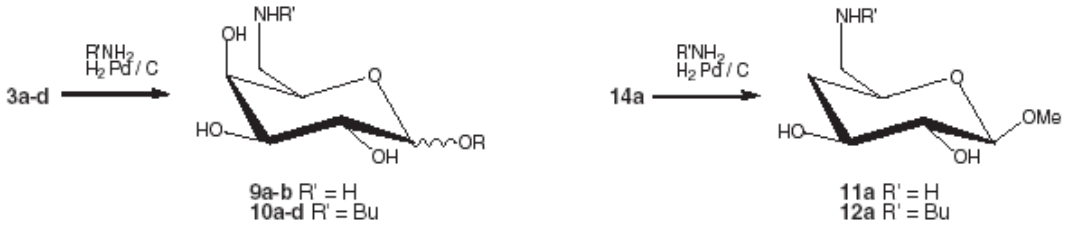
Scheme 1. Enzymatic oxidation of D-galactose [5,6].



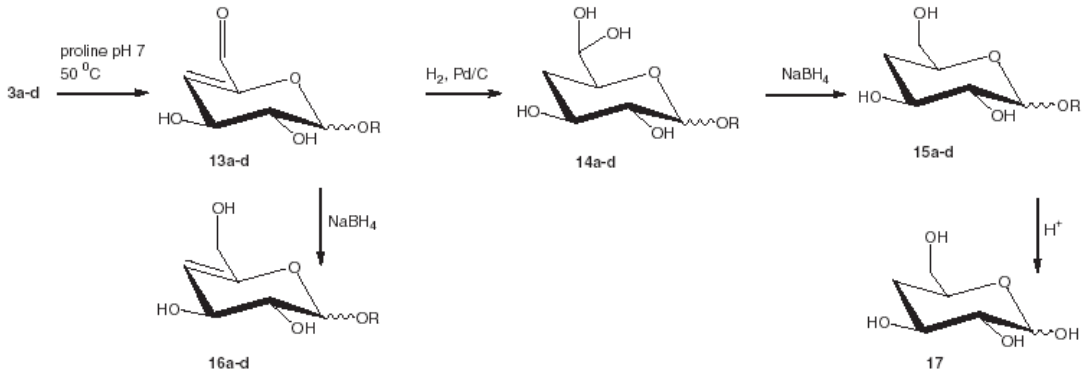
Scheme 2. Enzymatic oxidation of D-galactose derivatives.



Scheme 3. Synthesis of galacturonic and glucuronic acid derivatives.



Scheme 4. Synthesis of aminodeoxy sugar derivatives.

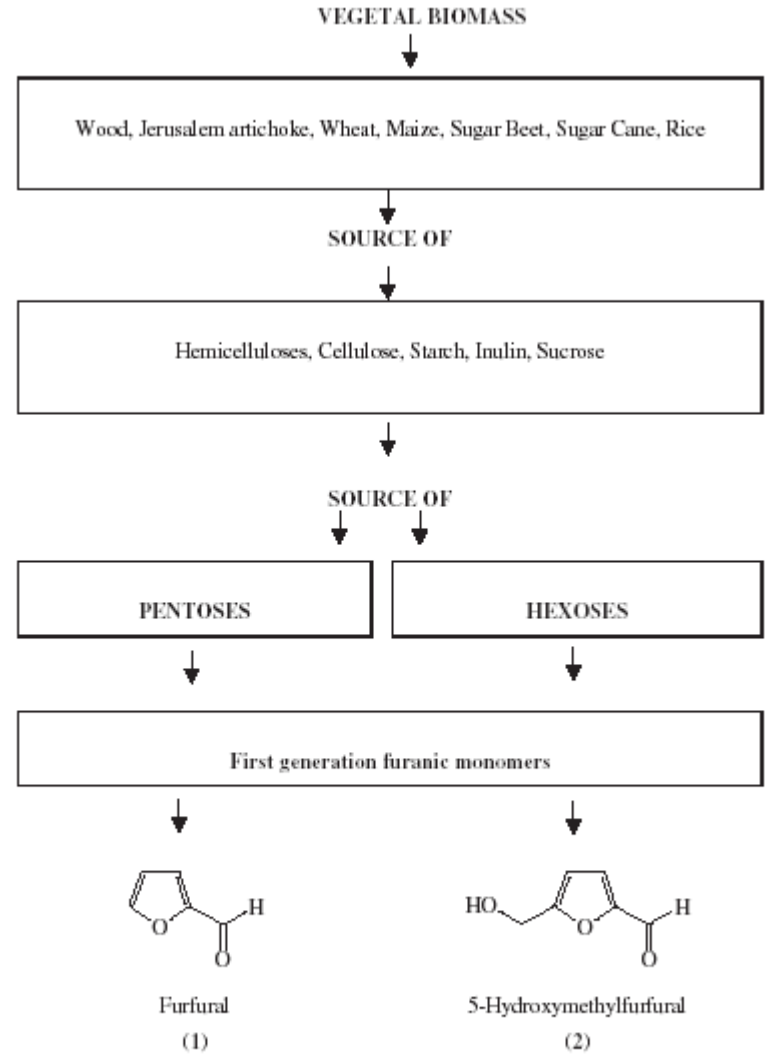


Scheme 5. Synthesis of 4-deoxy-D-glucose sugars.

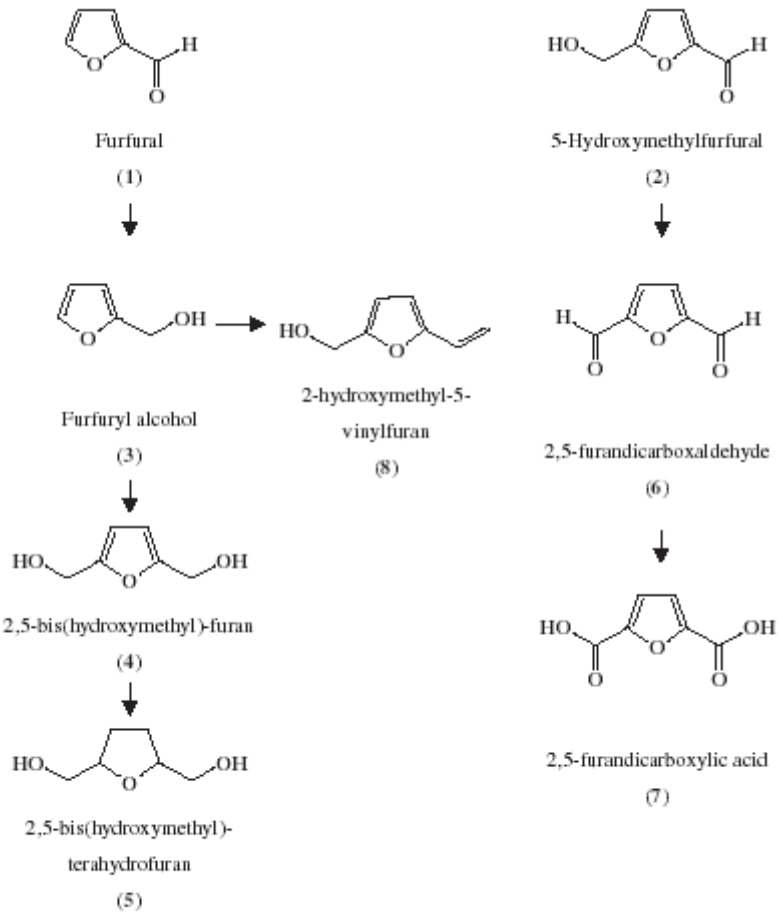
Recent catalytic advances in the chemistry of substituted furans from carbohydrates and in the ensuing polymers

C. Moreau, M.N. Belgacem, A. Gandini

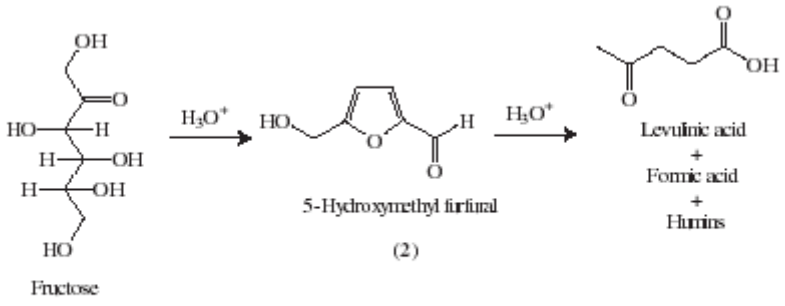
In this review, an overview is given on the last development of catalytic methods for the preparation of substituted furans from carbohydrates and ensuing polymers. The review starts with the recent aspects in the synthesis of some key furan monomers in the presence of solid catalysts. In the second part, selected examples are given of polymerization systems leading to furan-based materials with promising properties, thus constituting a serious alternative to petroleum-based counterparts. Finally, a short examination is given on what could be the future of furan chemistry with the recent development of ionic liquids as solvents.



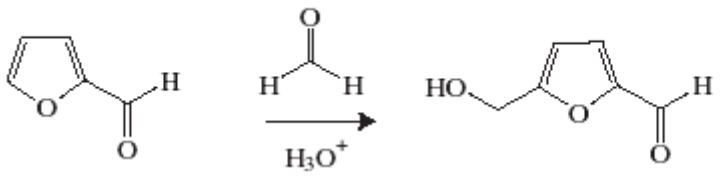
Scheme 1. From vegetal biomass to furfural (**1**) and hydroxymethyl-furfural (**2**), the two first-generation furanic monomers.



Scheme 2. Some of key furan derivatives.

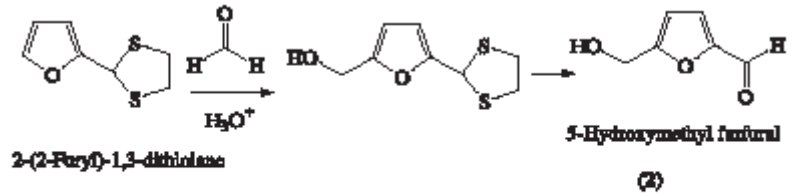


Scheme 3. Simplified reaction scheme for the dehydration of fructose.



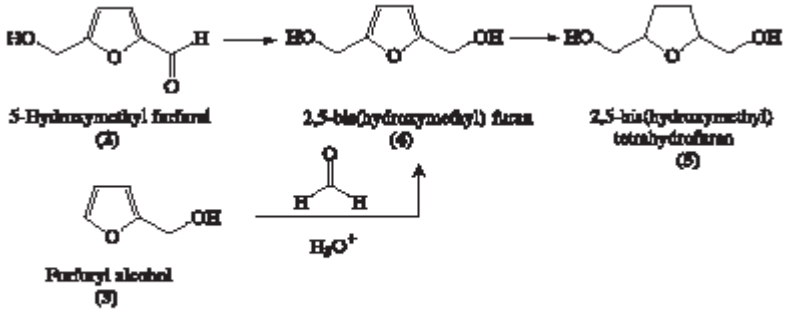
Furfural (1a) 5-Hydroxymethyl furfural (2)

Scheme 4. Simplified reaction scheme for hydroxymethylation of furfural.



2-(2-Furyl)-1,3-dithiolane 5-Hydroxymethyl furfural (2)

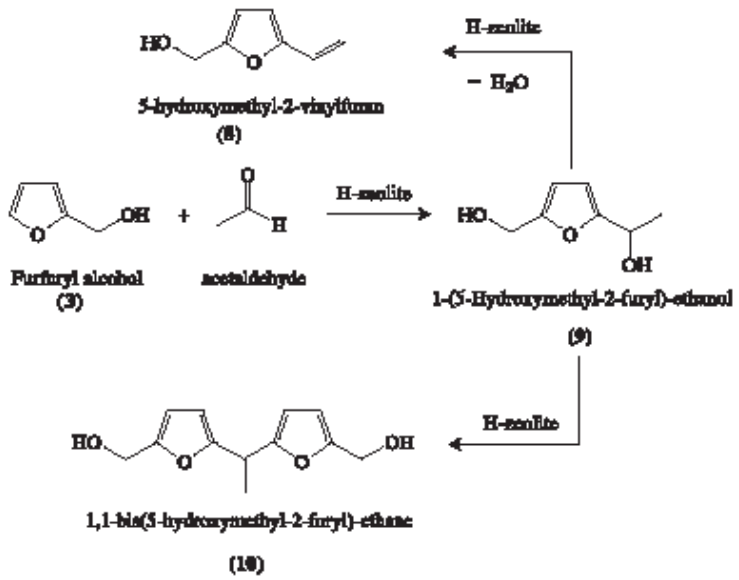
Scheme 5. Selective route to 5-hydroxymethylfurfural after protection and deprotection steps.



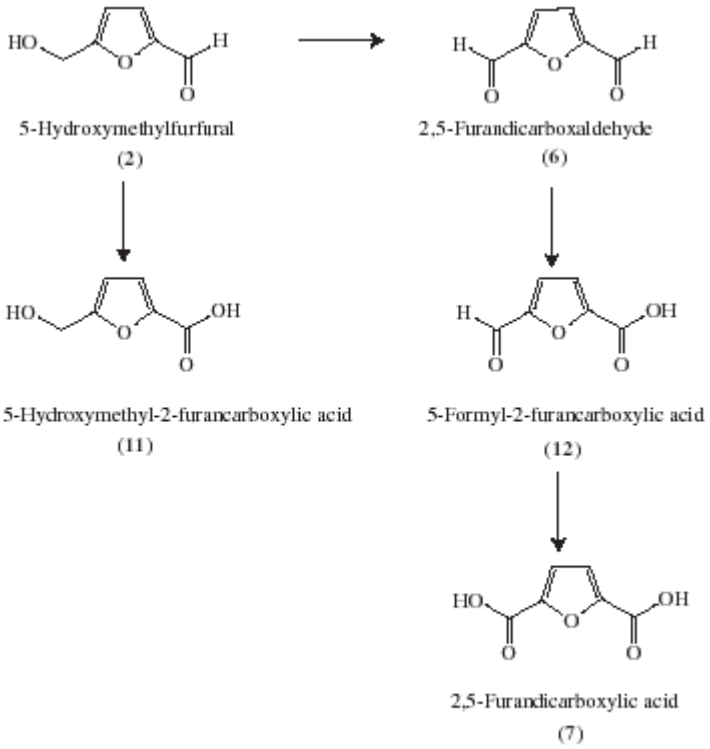
5-Hydroxymethyl furfural (2) 2,5-bis(hydroxymethyl) furan (4) 2,5-bis(hydroxymethyl) tetrahydrofuran (5)

Furfuryl alcohol (3)

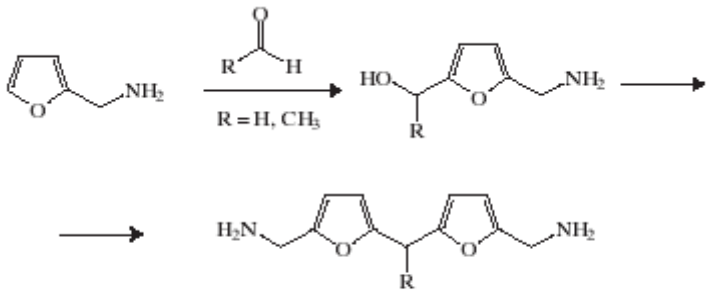
Scheme 6. Routes to 2,5-bis(hydroxymethyl)-furan.



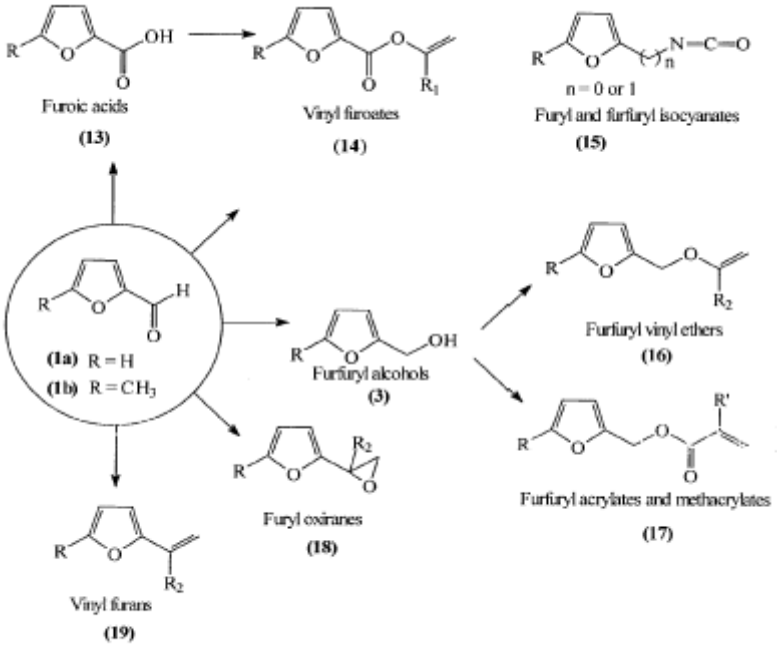
Scheme 7. Reaction scheme for hydroxyethylation of furfuryl alcohol with aqueous acetaldehyde.



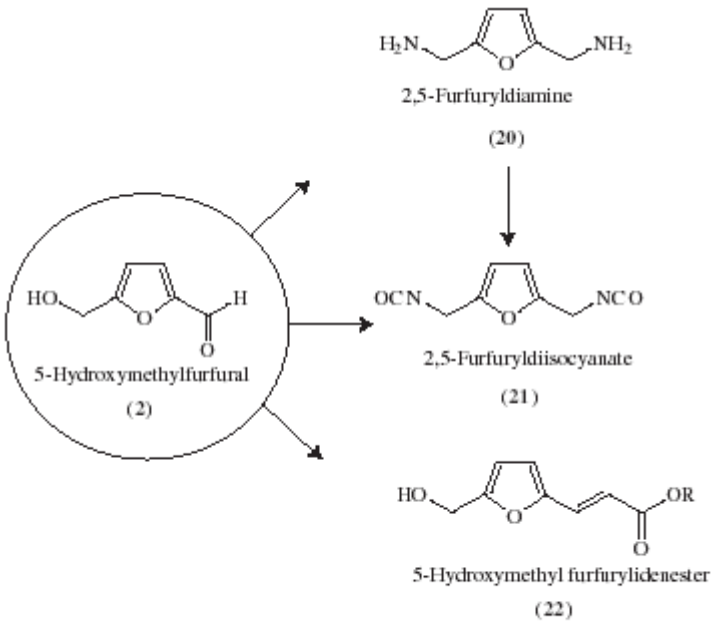
Scheme 8. Reaction scheme for the oxidation of 5-hydroxymethyl-furfural.



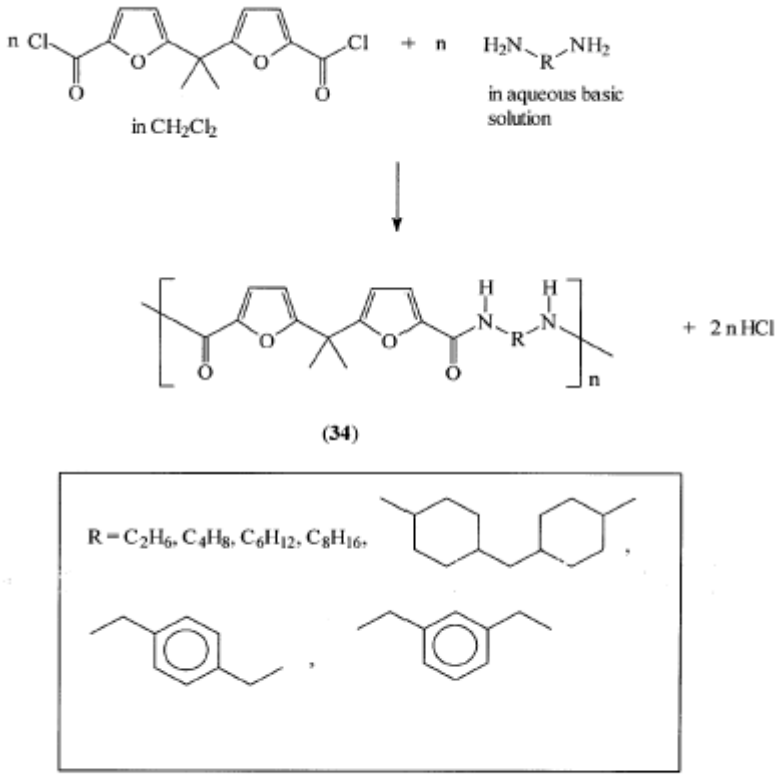
Scheme 9. Reaction scheme for hydroxyalkylation of furfurylamine.



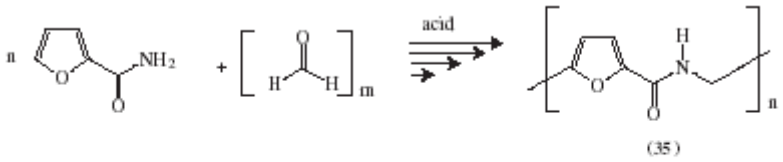
Scheme 10. Furfural and its derivatives.



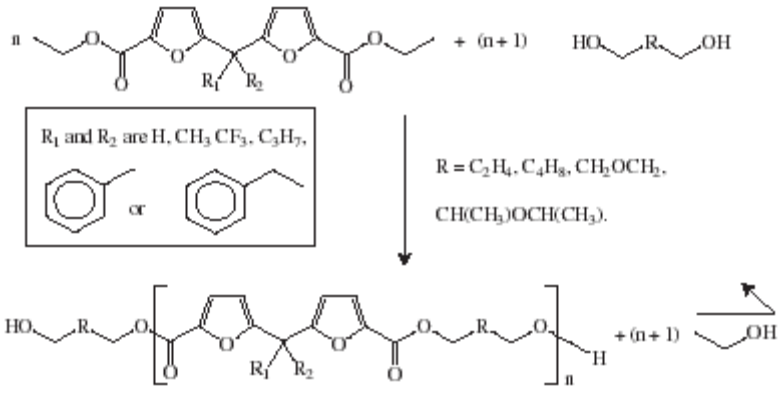
Scheme 11. Hydroxymethylfurfural and its derivatives.



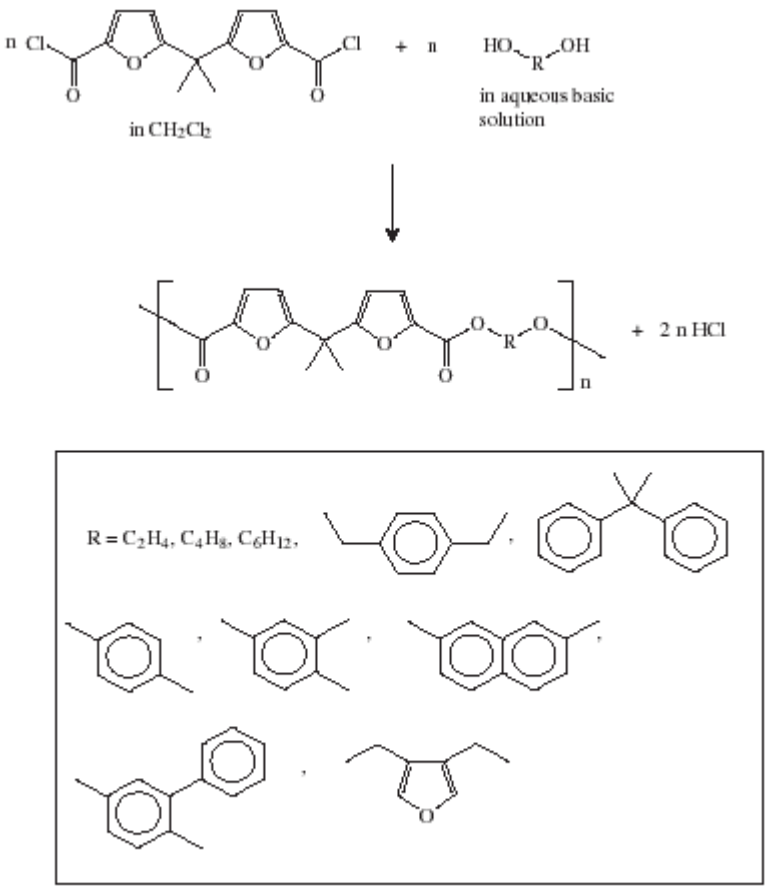
Scheme 12. Phase transfer-catalyzed polycondensation of furan polyacid chlorides with diamines.



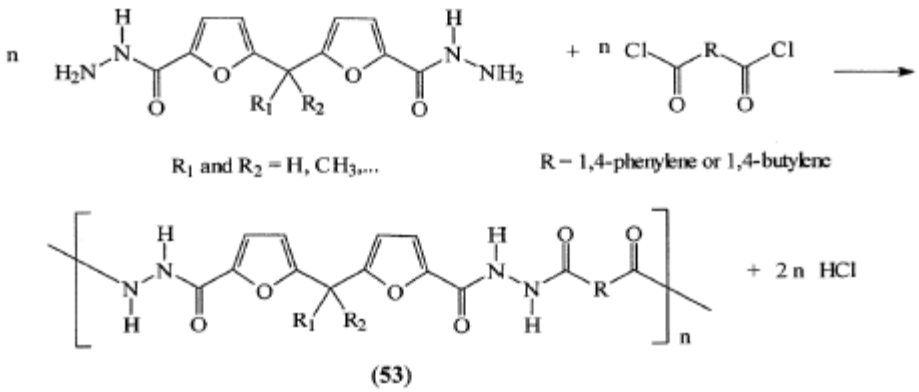
Scheme 13. Acid-catalyzed polycondensation of 2-furamide with paraformaldehyde.



Scheme 14. Polytransesterification of furan polyesters with diols.

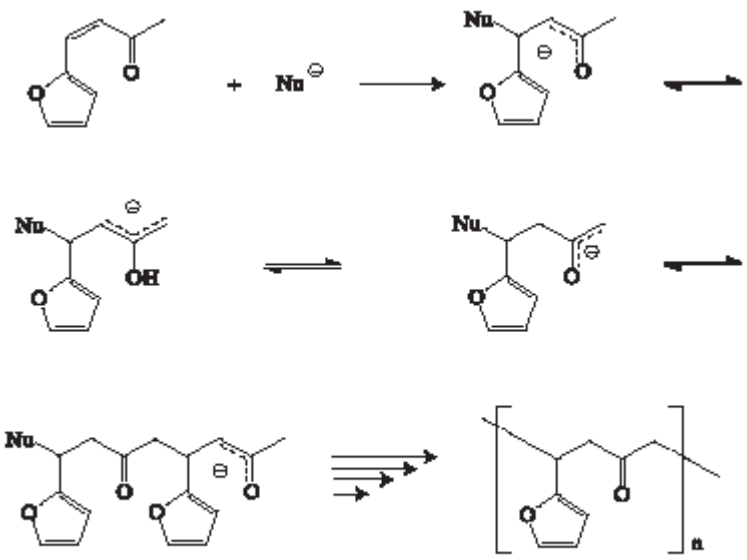


Scheme 15. Polycondensation of furan polyacid chlorides with diols.

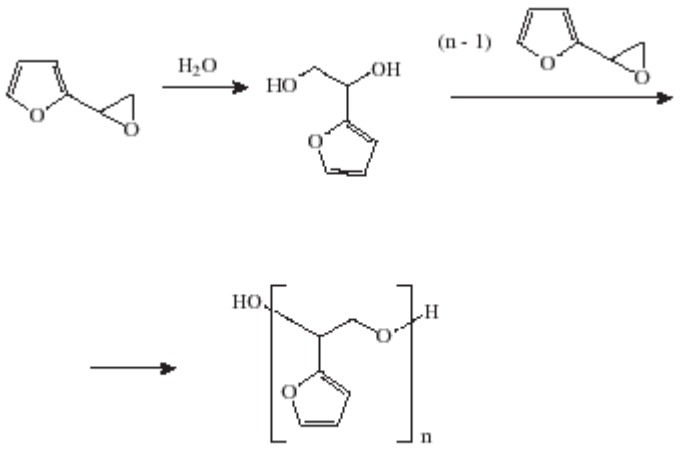


(53)

Scheme 16. Polycondensation of furan polyamides with diacid chlorides.



Scheme 17. Anionic polymerization of furfurylidene acetone.

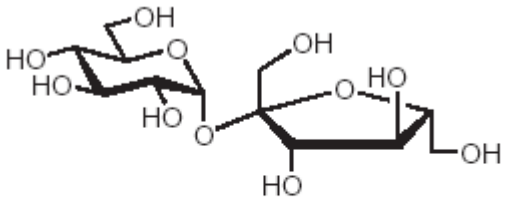


Scheme 18. Anionic polymerization of furyl oxirane (**18**).

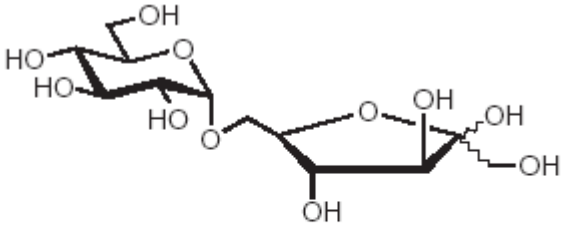
Oxidation of two major disaccharides: sucrose and isomaltulose

S. Trombotto, E. Violet-Courtens, L. Cottier, Y. Queneau

The chemical oxidation of sucrose, isomaltulose and methyl isomaltuloside is described, with special focus on the use of the NaOCl-TEMPO oxidizing system.



1 Sucrose



2 Isomaltulose

Scheme 1. Sucrose (**1**), Isomaltulose (**2**).

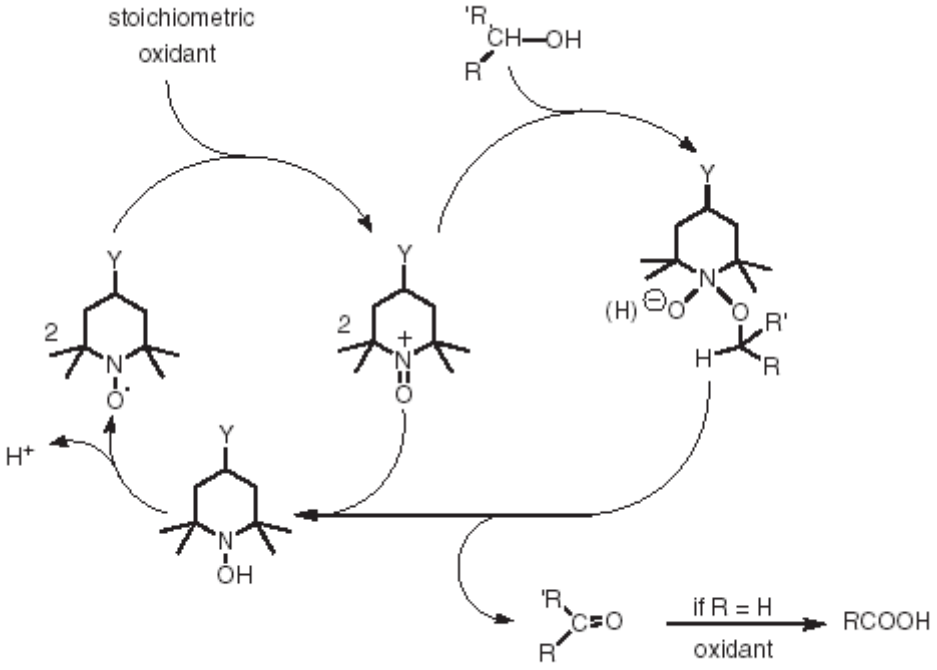
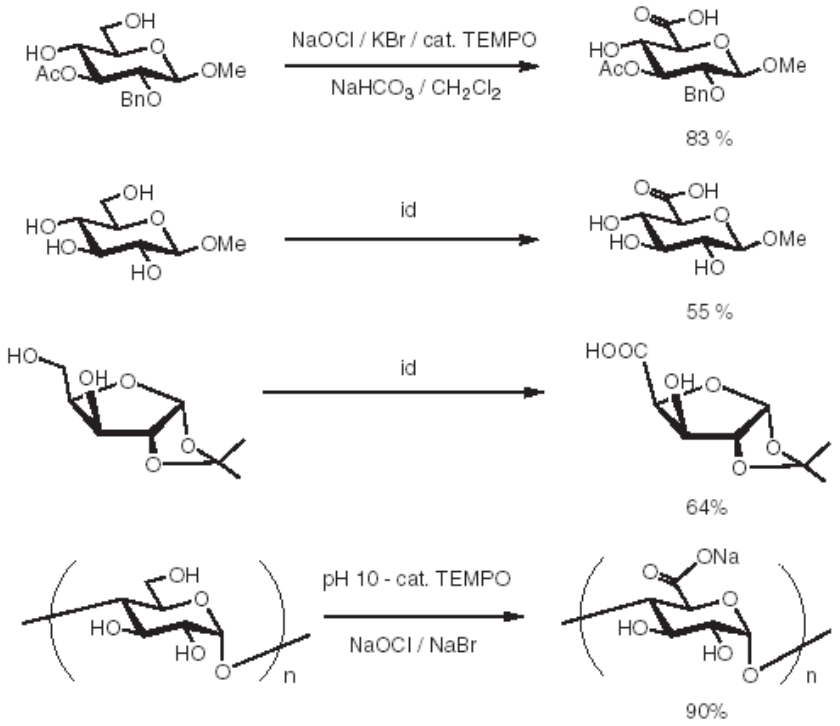
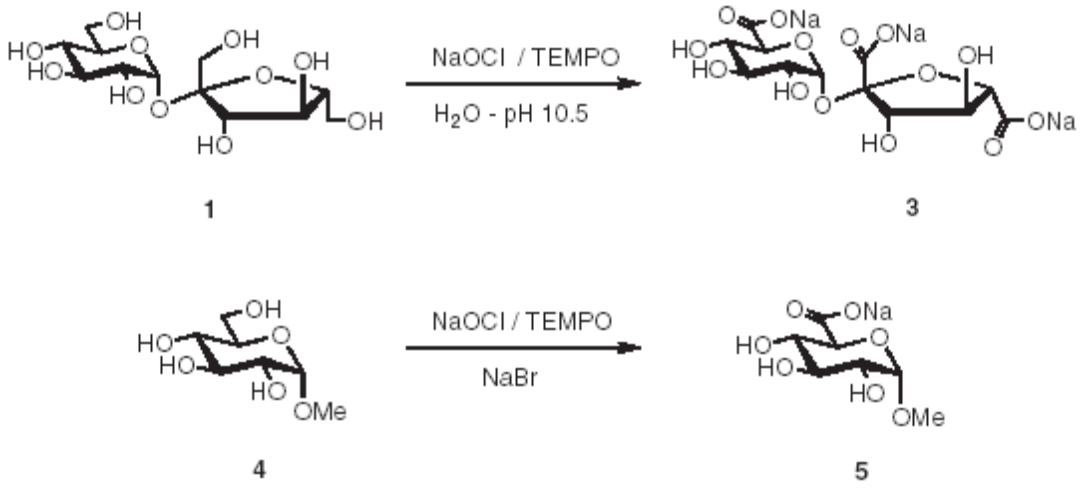


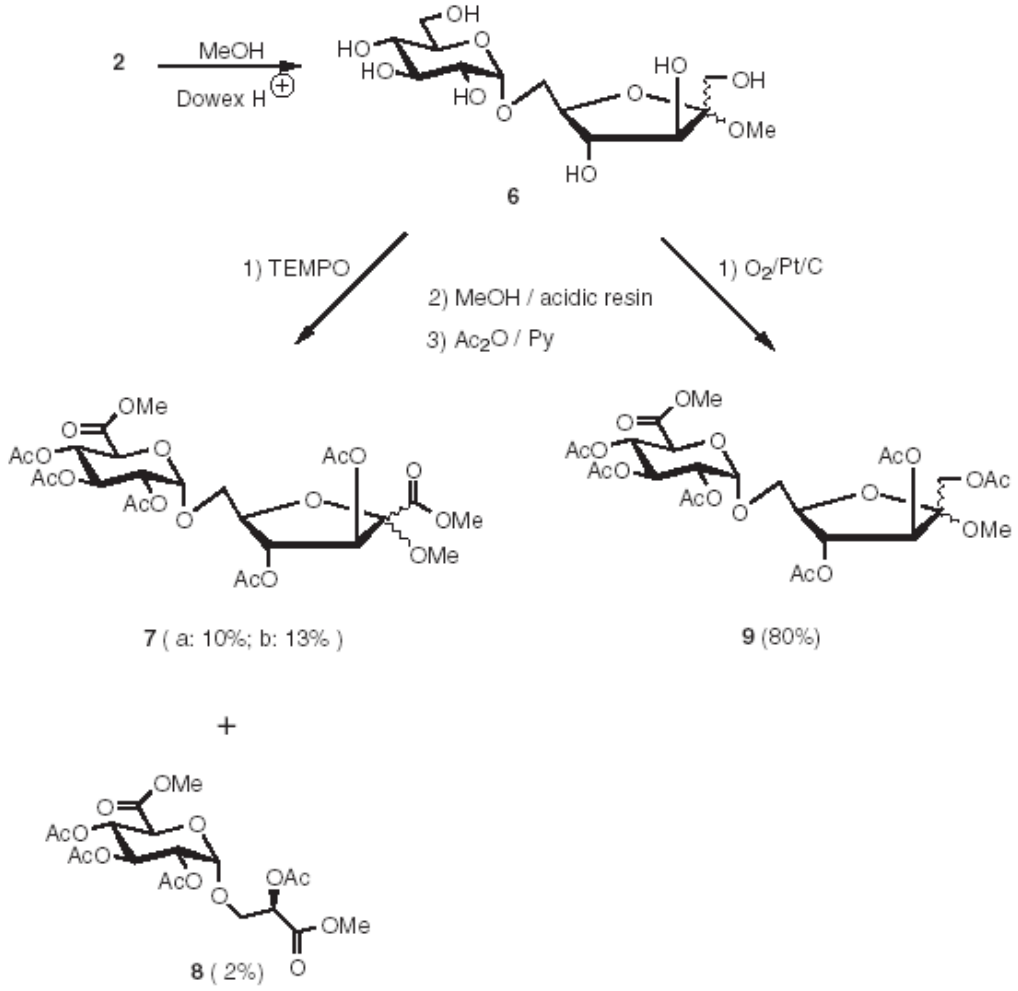
Figure 1. Reaction steps in TEMPO catalyzed alcohol oxidation.



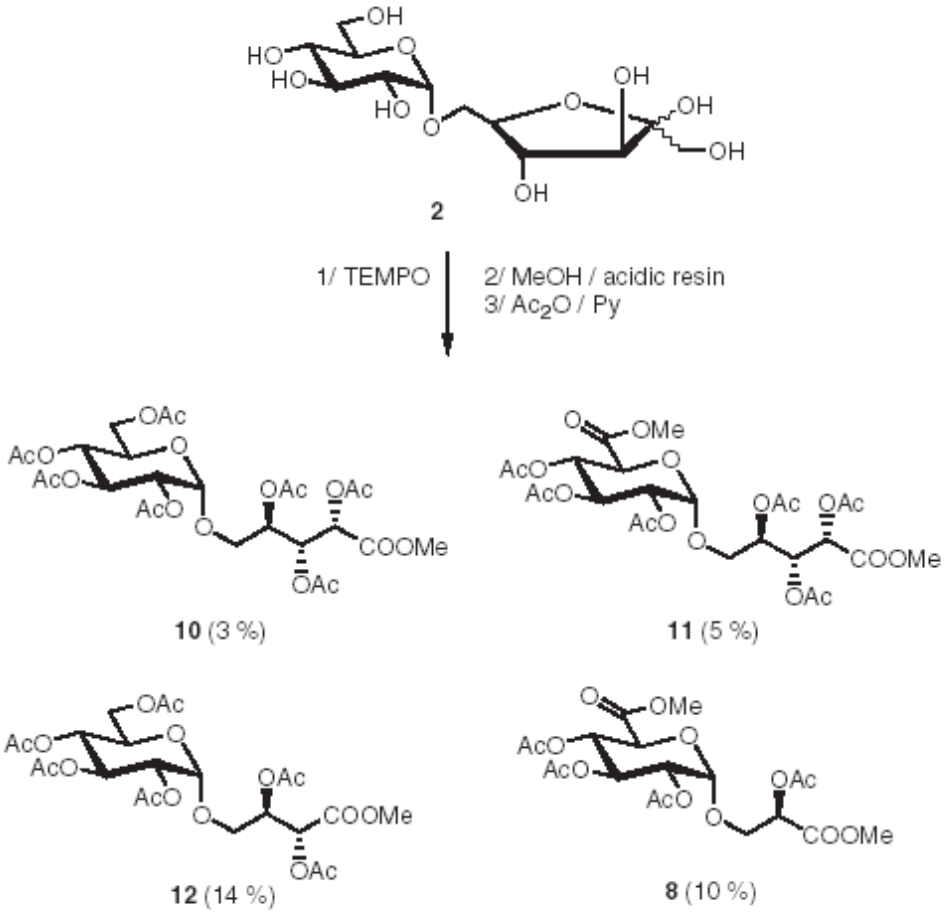
Scheme 2. Examples of TEMPO mediated oxidation of monosaccharides and polysaccharides [16–18].



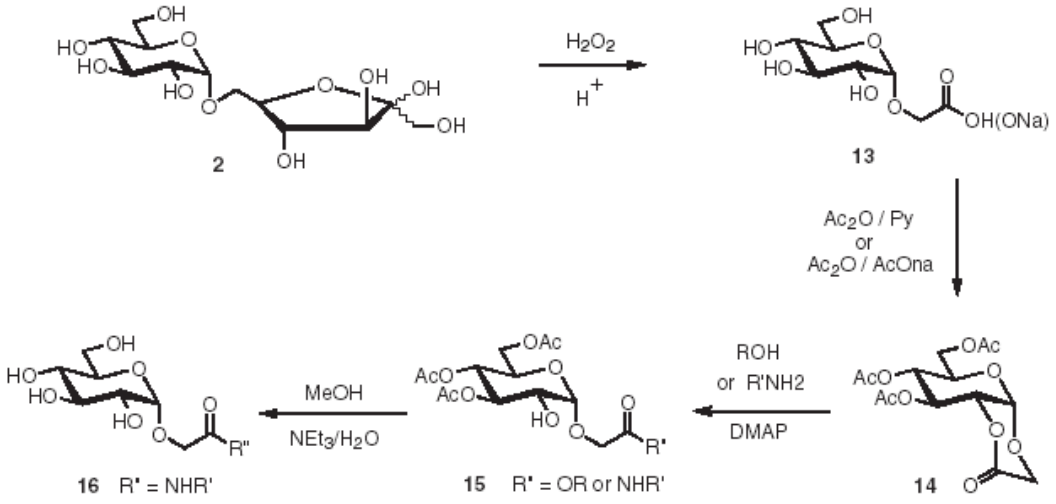
Scheme 3. Oxidation of sucrose [11] and methyl α-D-glucoside [25].



Scheme 4. Oxidation of methyl isomaltuloside with TEMPO or O_2/Pt/C [12].



Scheme 5. Oxidation of isomaltulose with TEMPO [12].



Scheme 6. Oxidation of isomaltulose with H_2O_2 [99].

Improved synthesis and physicochemical properties of alkoxylated inulin
T.M. Rogge et al.

Inulin, a polydisperse reserve polysaccharide extracted from chicory, has been modified by alkoxylation in a water-free medium using a basic catalyst. The reaction of inulin with ethylene oxide, as well as propylene oxide, was performed in an organic solvent, N-methylpyrrolidinone, with triethylamine as basic catalyst in almost quantitative yields. The reaction resulted in a range of products with very specific properties such as highly increased water solubility, moderate surface activities and very high cloud points in electrolyte media.

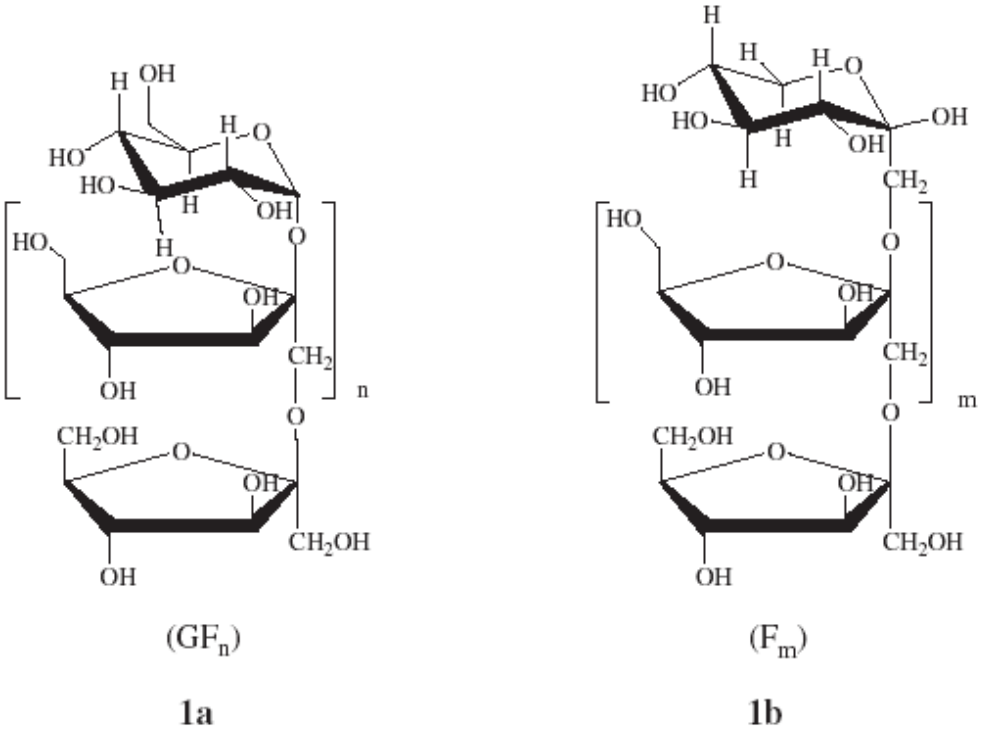


Figure 1. Structure of inulin in the GF_n and in the F_m form.

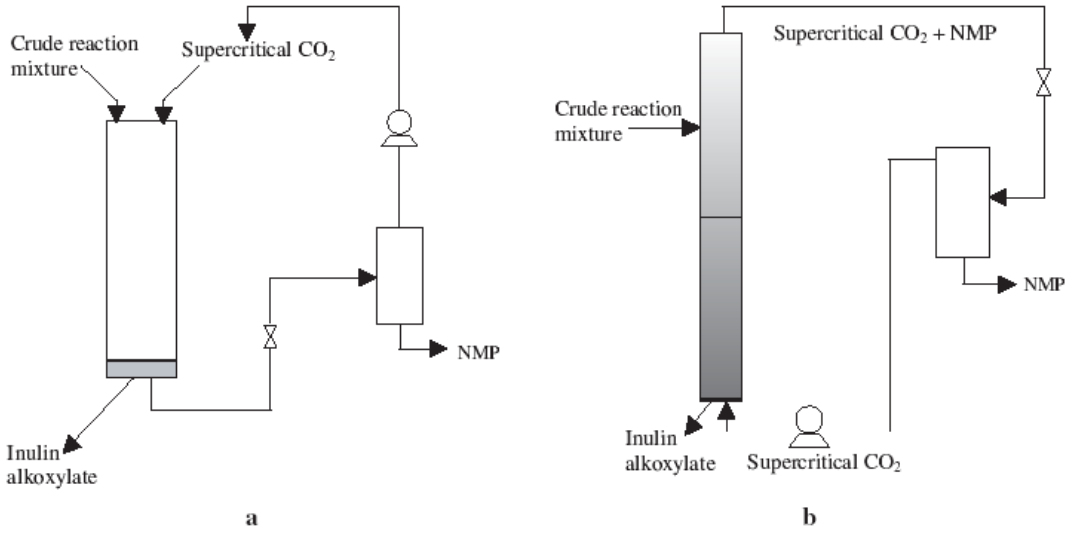


Figure 2. Solid/liquid (a) and liquid/liquid, (b) supercritical CO_2 extraction.

Table 1
Overview of the synthesized inulin derivatives

Equiv. Et_3N	Equiv. EO	Equiv. PO	Delta viscosity (cSt)
0.01	1.5	–	−488
0.03	1.5	–	−1111.5
0.1	0.5	–	1383
0.1	1.0	–	1907
0.1	1.5	–	996
0.1	2.0	–	514
0.1	3.0	–	−422
0.1	4.0	–	−126.8
0.1	5.0	–	−847.1
0.1	6.0	–	−1229
0.1	7.0	–	−525
0.1	8.0	–	−564.6
0.1	9.0	–	−1233.1
0.1	10.0	–	−1025
0.1	20	–	−920.8
0.1	44.7	–	−268
0.3	0.5	–	23 686
0.3	1.5	–	12 711
0.1	–	0.5	2369
0.1	–	1.0	1468
0.1	–	2.0	366
0.1	5.0[a]	4.0[a]	−588
0.1	20.0[a]	4.0[a]	716
0.1	4.0[b]	4.0[b]	634
0.1	6.0[b]	5.0[b]	902

[a]Ethoxylation after propoxylation, without purification in-between.
[b]Propoxylation after ethoxylation, without purification in-between.

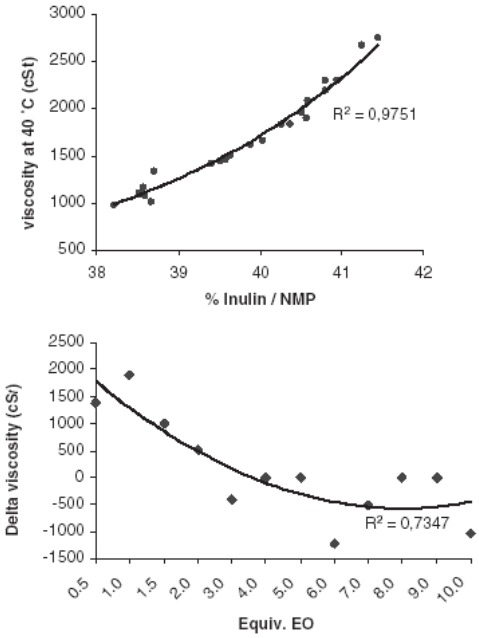


Figure 3. Viscosity of inulin and inulin ethoxylates in NMP.

the reactor when ethylene oxide is added too fast. The

Table 2
Results of the acid hydrolysis of inulin ethoxylates

Equiv. Et_3N	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Equiv. EO	0.5	1	1.5	20				0.5
Equiv. PO					0.5	1	2	1
DS[a]	0.43	0.68	0.66	0.98	0.44	0.70	0.94	0.53

[a]The DS was calculated from the amount of free glucose and free fructose after hydrolysis.

Table 3
Influence of the amount of catalyst used on the degree of substitution

Equiv. Et_3N	0.01	0.03	0.1	0.3
Equiv. EO	1.5	1.5	1.5	1.5
DS[a]	0.71	0.75	0.82	0.85

[a]The DS was calculated from the amount of free glucose and free fructose after hydrolysis.

Table 4
Results of the MALLS analysis of inulin alkoxylates synthesized with 0.1 equivalent of Et_3N

Inulin derivative	Molecular weight (Da)		MS
	Estimated[a]	Result of MALLS	
Inutec® N25	5 283	5 279	–
0.5 equiv. EO	5 980	6 078	0.56
1.0 equiv. EO	6 695	6 575	0.90
20 equiv. EO	33 865	29 130	16.63

[a]The estimated molecular weight was calculated on the basis of the average molecular weight of inulin and the expected degree of substitution.

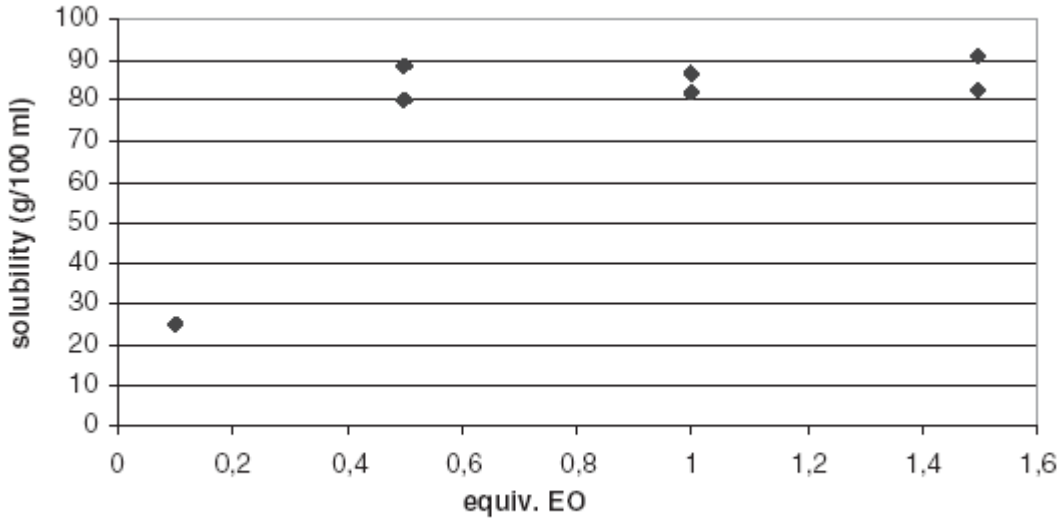


Figure 4. Solubility of alkoxylated inulin in water at room temperature.

Table 5
Surface tensions of 1% (w/v) solutions of inulin alkoxylates according the du Nouy ring method at 20 °C

Equiv. Et_3N	Equiv. PO	Equiv. EO	γ (mN/m)
0.01	–	1.5	60
0.03	–	1.5	53.9
0.1	–	1	56.7
0.1	–	2	63.3
0.1		6	57.6
0.1	0.5	–	53.2
0.1	1.0	–	62.1
0.1	2.0	–	51.0
0.1	4.0	–	56.7
0.1	4	5	48.3
0.1	4	20	54.1
0.1	4	40	57.6
0.3	–	0.5	57.5
0.3	–	1.5	64.6

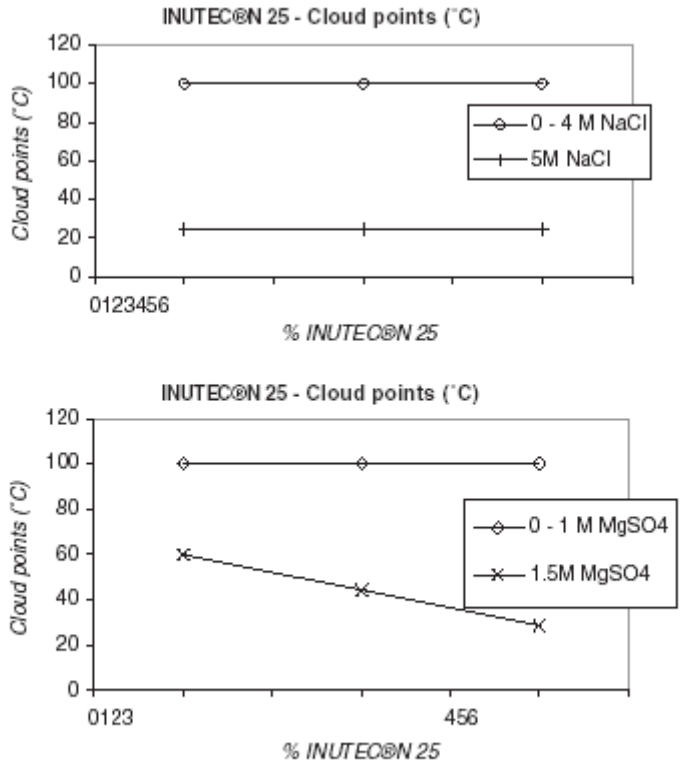


Figure 5. Cloud points of native inulin in electrolyte medium.

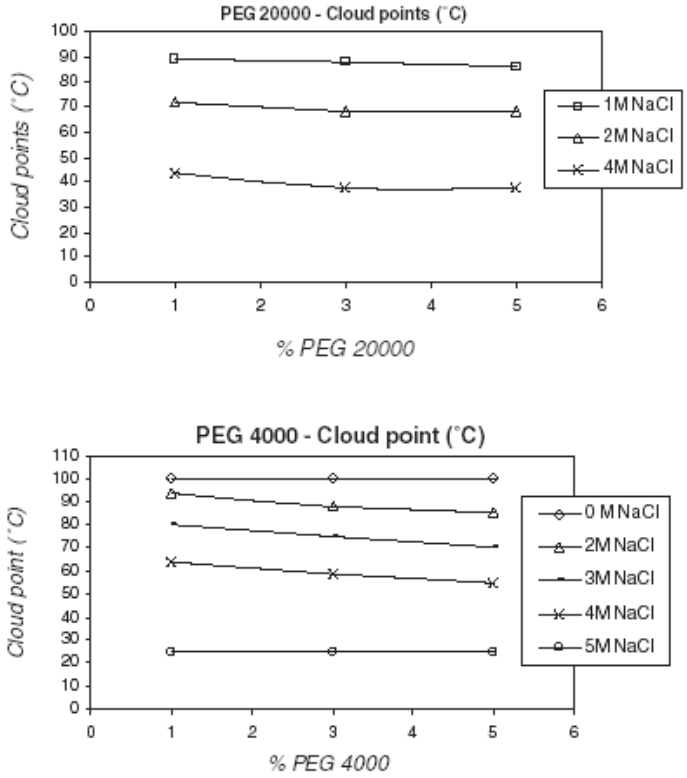


Figure 6. Cloud points of PEG 4000 and PEG 20000 in electrolyte medium with different concentrations.

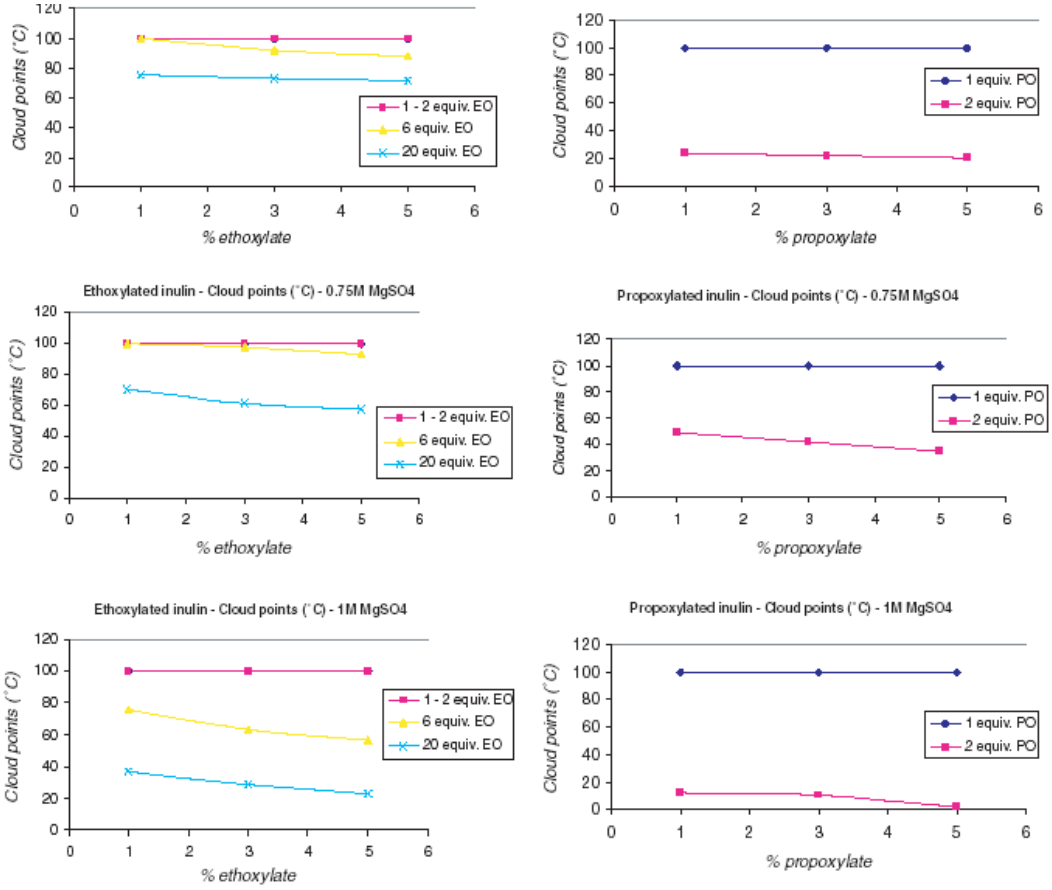
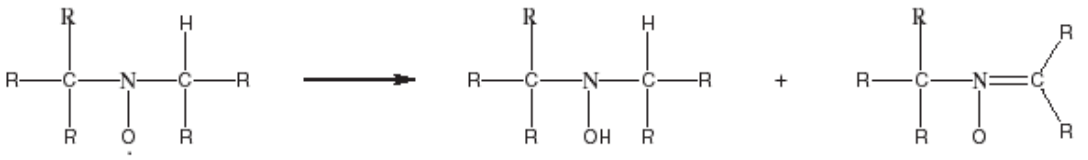


Figure 7. Cloud points of some inulin ethoxylates and propoxylates in electrolyte media.

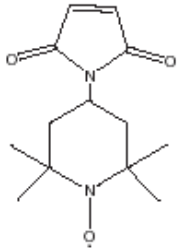
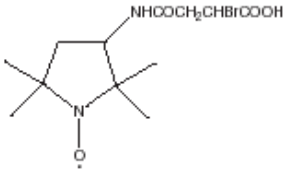
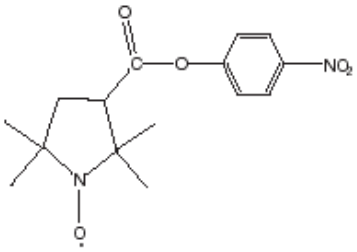
TEMPO-mediated oxidation of polysaccharides: survey of methods and applications
P.L. Bragd et al.

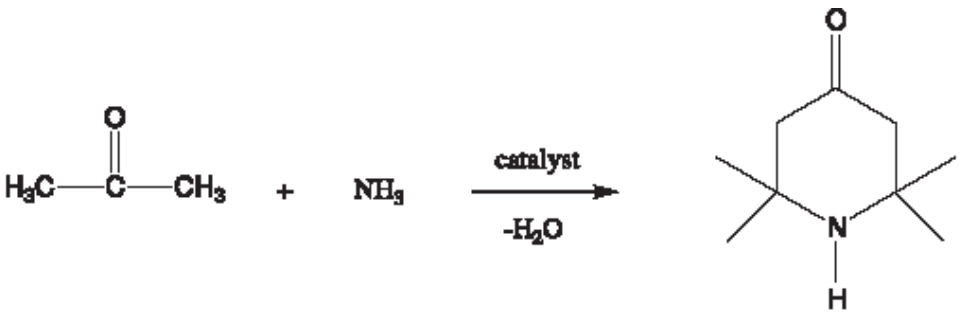
This review deals with TEMPO as a catalyst in oxidation of alcohol functions in polysaccarides. Synthesis of TEMPO and derivaties and the mechanism of the oxidative cycle in which TEMPO in involved in oxidation of alcohols are discussed. Results of oxidation of various polysaccarides with respect to yield, and introduction of the functional groups (aldehyde and/or carboxylate) are presented. Most of the primary oxidants are not ideal, as they produce large amounts of salts, e.g., sodium choride from sodium hypochlorite. Results and perspectives are given to change the salt-based oxidative systems for much cleaner oxygen or hydrogen peroxide/enzyme-based TEMPO systems. Moreover, several immoblized TEMPO systems have been developed.



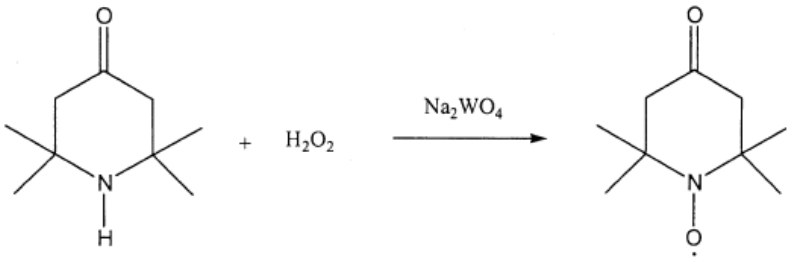
Scheme 1. Disproportionation of nitroxyls into hydroxylamine and nitrone.

Table 1
Some biological systems using nitroxyl radicals as spin labeling agents

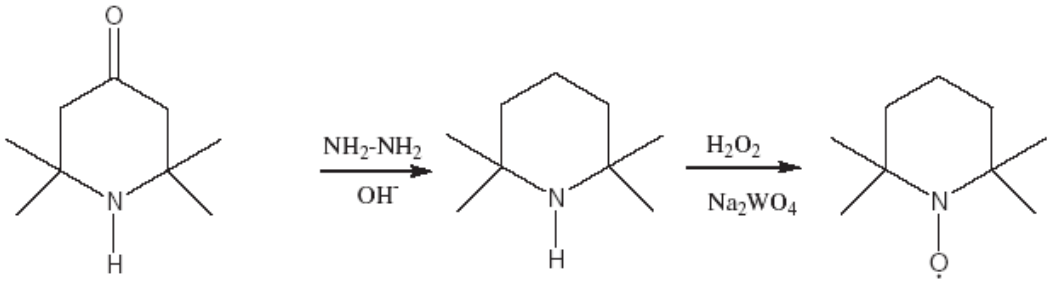
Entry	Biological component	Spin label	References
1	Hemoglobin		[27]
2	Ribonuclease A		[28]
3	α-Chymotrypsin		[29]



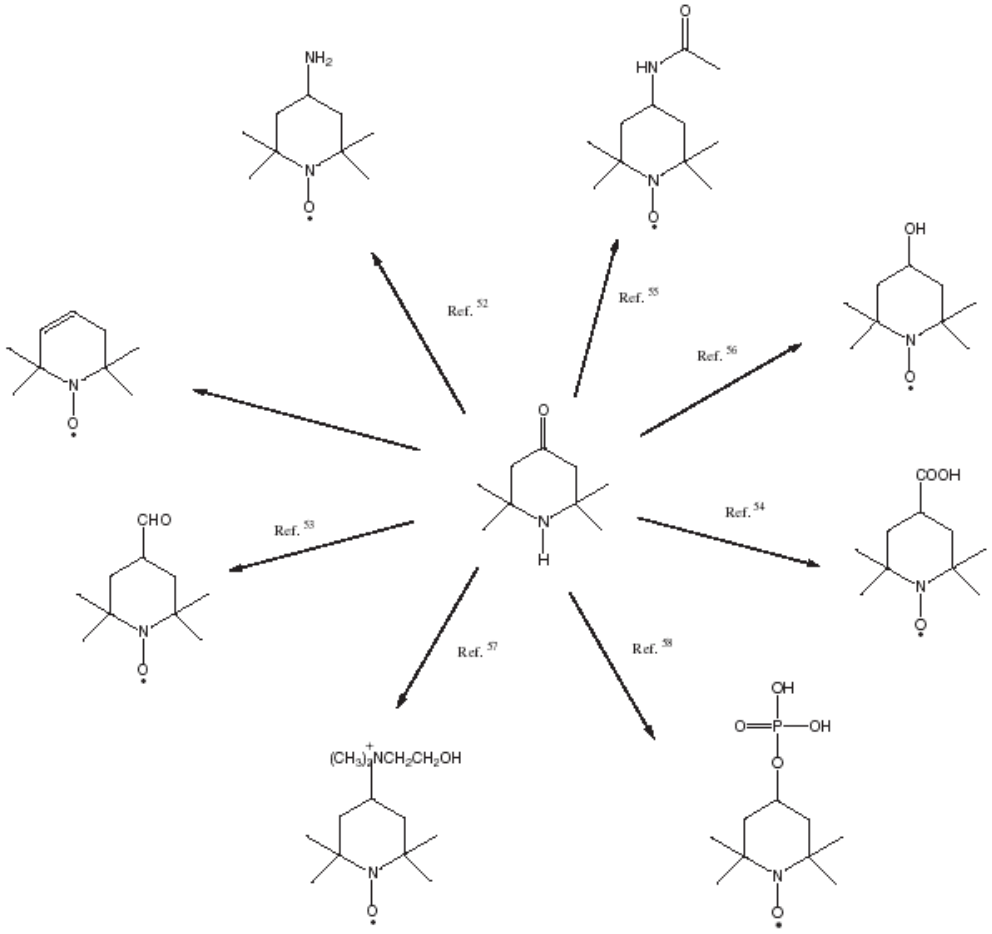
Scheme 2. Synthesis of triacetoneamine by aldol condensation of acetone and ammonia.



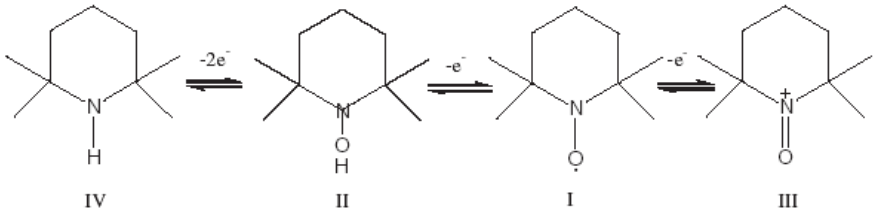
Scheme 3. Oxidation of triacetoneamine to 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl by sodium tungstate/hydrogen peroxide.



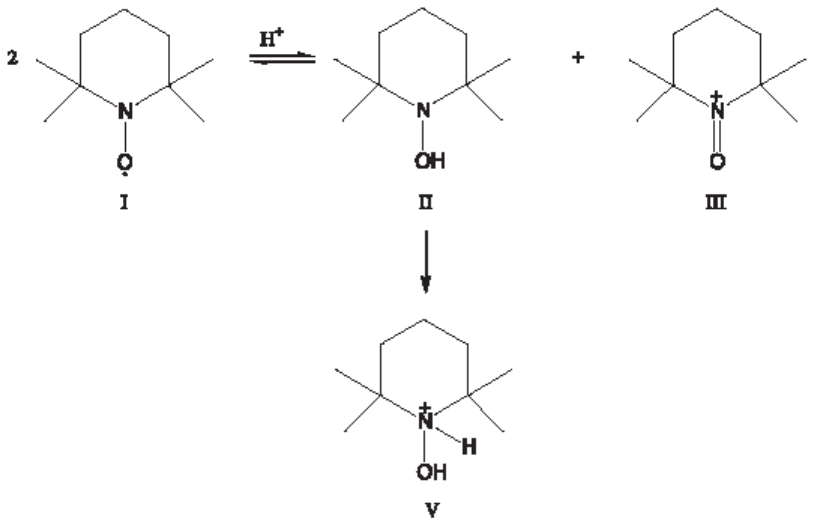
Scheme 4. TEMPO synthesis.



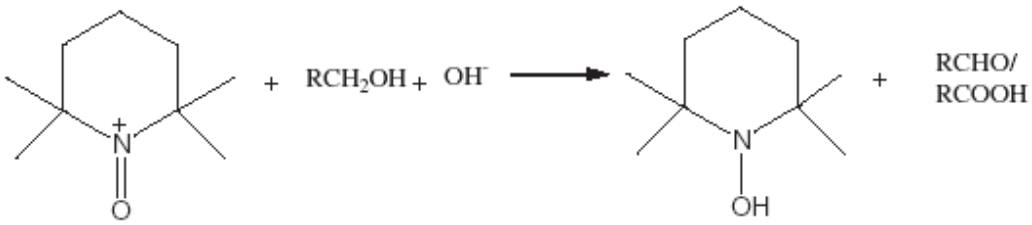
Scheme 5. 4-substituted TEMPO derivatives prepared from triacetoneamine.



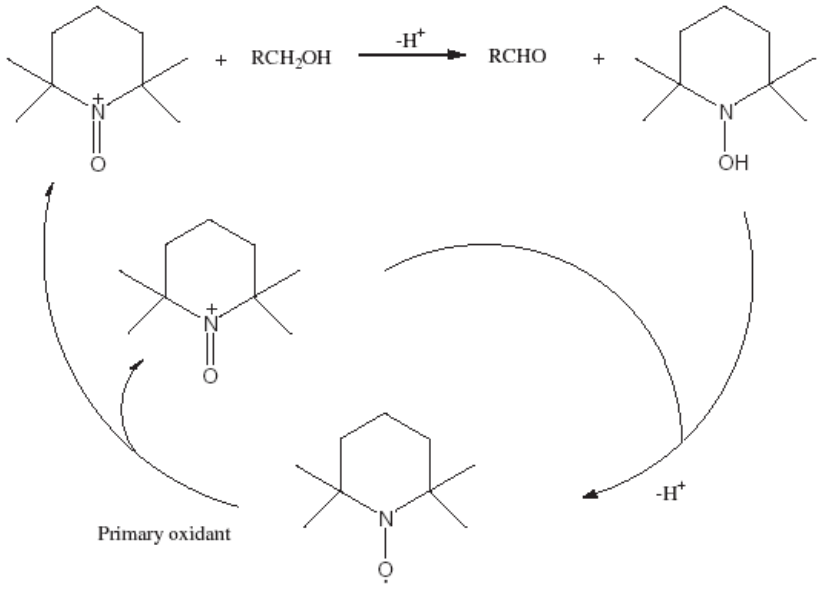
Scheme 6. TEMPO (I) and the corresponding members of the redox series (amine) (IV), hydroxylamine (II), nitrosonium ion (III) and amine (IV).



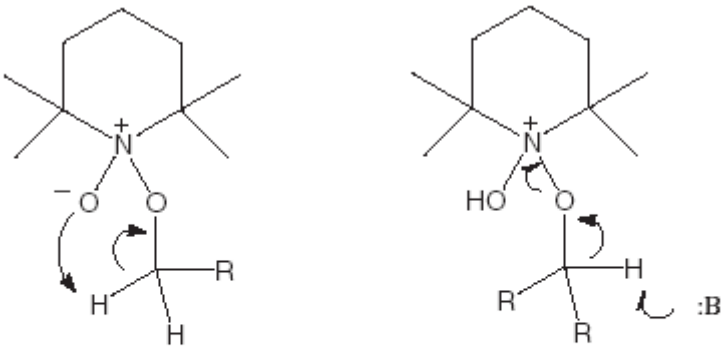
Scheme 7. TEMPO-radical disproportionation under acidic conditions to the nitrosonium ion (III) and the protonated hydroxylamine (V).



Scheme 8. Oxidation of alcohols by the nitrosonium salt under alkaline conditions.

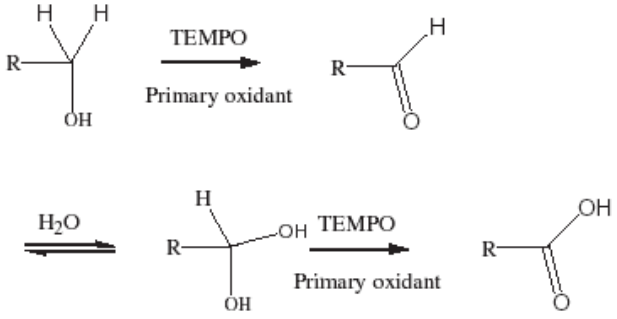


Scheme 9. A simplified mechanism for the catalytic cycle in TEMPO-mediated oxidation of alcohol substrates under weakly alkaline conditions. The TEMPO radical is continuously regenerated *in situ* by reaction of the nitrosonium ion and the hydroxylamine.

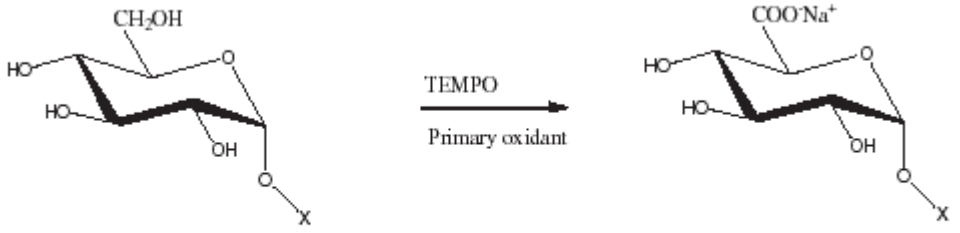


VI VII

Scheme 10. Proposed mechanistic adducts in alkaline (VI) and acidic conditions (VII).

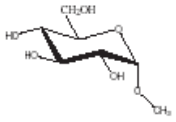
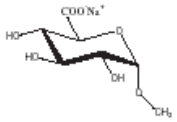
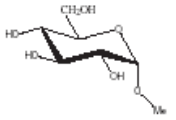
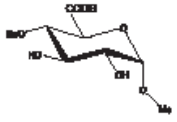
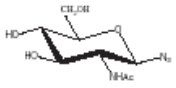
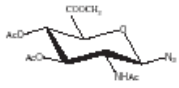
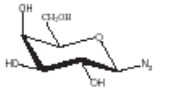
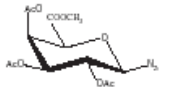
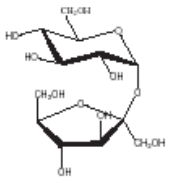
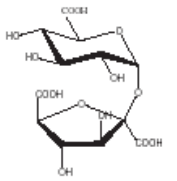


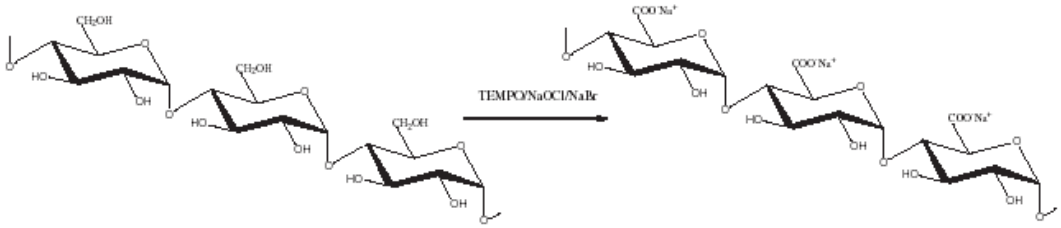
Scheme 11. TEMPO-mediated oxidation of primary alcohols to carboxyl via the hydrated (*gem*-diol) aldehyde intermediate.



Scheme 12. TEMPO oxidation of the primary hydroxyl group in anomeric-protected glucose.

Table 2
TEMPO-mediated oxidation of mono- and disaccharides using different hypohalites as primary oxidant systems

Entry	Substrate	Product	Conditions	Yield	References
1			(a) NaOCl/NaBr (b) NaOCl/ultrasound (c) NaOCl	> 95 82 > 90	[100] [106] [107]
2			1. Tribenzoylation 2. Methylation 3. Debenzoylation 4. NaOCl/NaBr/TEMPO	74	[111]
3			1. $Ca(OCl)_2$/KBr 2. Methylation 3. Acetylation	63	[110]
4			1. $Ca(OCl)_2$/KBr 2. Methylation 3. Acetylation	64	[110]
5			NaOCl/NaBr Ultrasound (500 kHz)	80	[106]

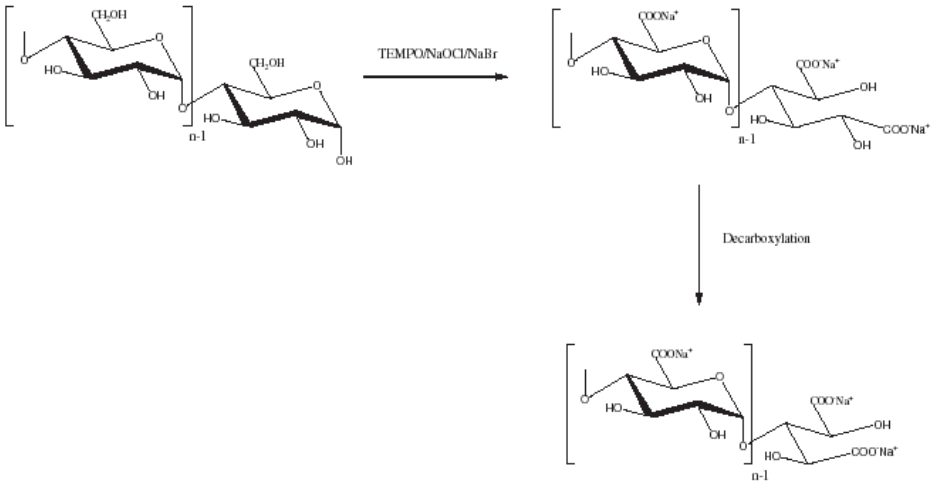


Scheme 13. TEMPO/NaOCl/NaBr oxidation of glucans (i.e., starch) to the corresponding polyuronic derivatives.

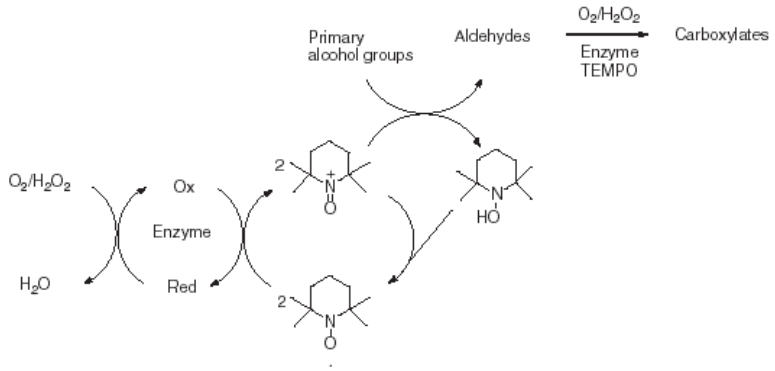
Table 3
Oxidation of polysaccharides by the TEMPO/hypochlorite/bromide system

Entry	Substrate	Conditions	Yield	References
1	Potato starch (Cold-water soluble)	NaOCl/NaBr	>95	[92,98–100]
2	Wheat starch (Cold-water insoluble)	NaOCl/NaBr	95	[113]
3	Potato amylose	NaOCl/NaBr	>95	[113]
4	Potato amylopectin	NaOCl/NaBr	95	[113]
5	Inulin	NaOCl/NaBr	87	[100,114]
6	Pullulan	NaOCl/NaBr	>95	[98,100]
7	Chitin (Crustacean)	NaOCl/NaBr	>90	[144]
8	Chitin (*A. niger*)	NaOCl/NaBr	45	[143]
9	Chitosan	NaOCl/NaBr	91	[113]
10	(α, β, γ) Cyclodextrin	NaOCl/NaBr	90	[122–124]
11	Mercerized cellulose[a]	NaOCl/NaBr	>95	[126,127]
12	Dissolved and regenerated cellulose[b,c]	NaOCl/NaBr	>95	[126,138]
13	Mercerized cellulose (bacterial)	NaOCl/NaBr	>95	[127,128]
14	Mercerized cellulose (Microcrystalline)	NaOCl/NaBr	>95	[126,127]
15	Cellulose[d]	NaOCl/NaBr	8	[128,129]
16	Hyaluronan	NaOCl/NaBr	100	[145]
17	Galactomannan	NaOCl/NaBr	66	[139]
18	Scleroglucan	NaOCl/NaBr	100	[140,141]

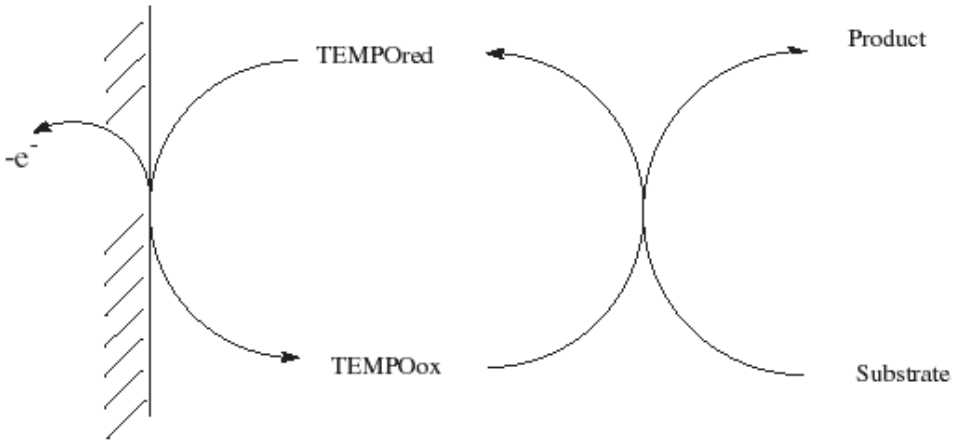
[a]Softwood-bleached kraft pulp.
[b]Prepared from linter cellulose using 0.5 M cupri-ethylenediamine.
[c]Prepared from wood cellulose pulp, using NMMO or phosphoric acid.
[d]Hardwood kraft pulp.



Scheme 14. Oxidation of maltodextrin to polyuronic acid by TEMPO/hypochlorite and sodium bromide. Terminal reducing units are transformed into dicarboxylic functionalities, which subsequently are decarboxylated.



Scheme 15. TEMPO-mediated oxidation of primary alcohol groups in carbohydrates to C-6-aldehydes and carboxylates using oxidative enzymes (e.g. laccase or peroxidase) in the presence of oxygen or hydrogen peroxide respectively as primary oxidant systems.



Scheme 16. Indirect electrode oxidation of organic substrates using TEMPO as mediator.