Serinol: a biosourced building block for better mechanical reinforcement and sustainable vulcanization of rubber compounds

Maurizio Galimberti

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Research on sustainable chemistry

ISCaMaP

Innovative Sustainable Chemistry and Materials and Proteomics Group

Research on sustainable chemistry. Key features

- ☞ Raw materials, from renewable sources, are easily available
- ☞ No impact on the food chain
- ☞ To use wastes and residues
- ☞ Syntheses according to principles of green and sustainable chemistry
- ☞ Good economic perspectives

ISCaMaP

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Objective of the research

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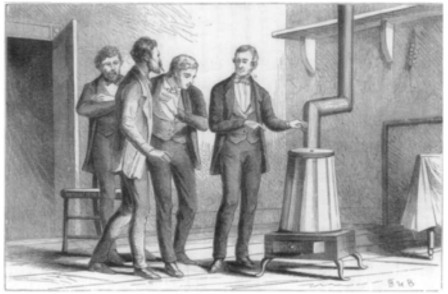
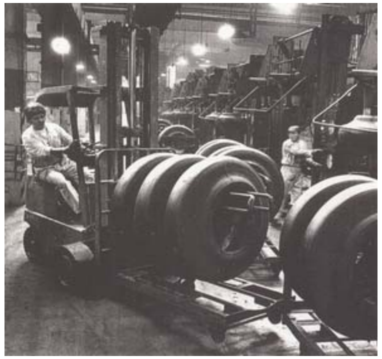
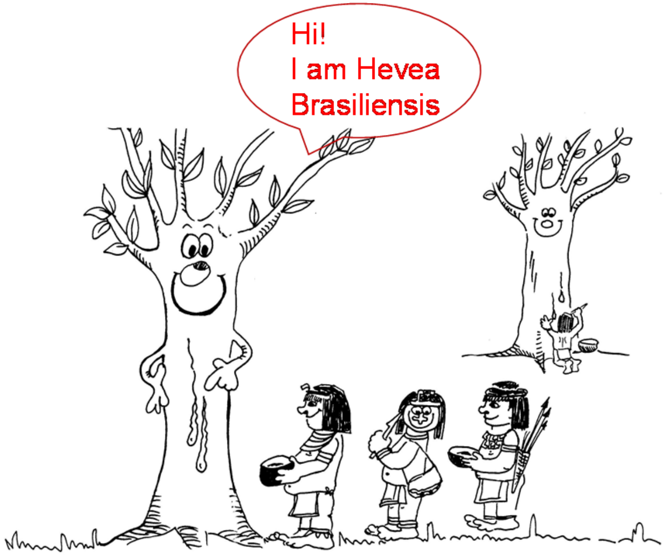


Quiringh Gerritsz. van Brekelenkam
A Cobbler at work, his wife spinning wool





☞ Sustainable chemistry and rubber technology

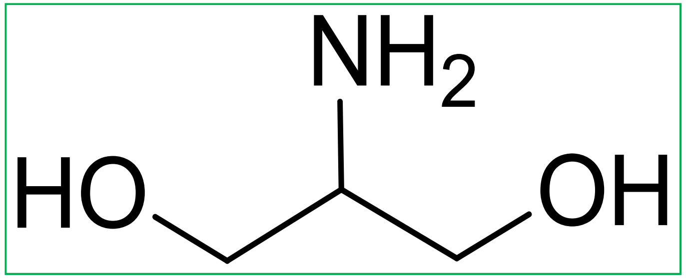
Outline of the presentation

- ☞ Selection of starting building block
- ☞ Synthesis of derivatives: control of reaction pathways
- ☞ Innovative chemicals for rubber compounds
- ☞ Mechanical reinforcement
- ☞ Vulcanization

Outline of the presentation

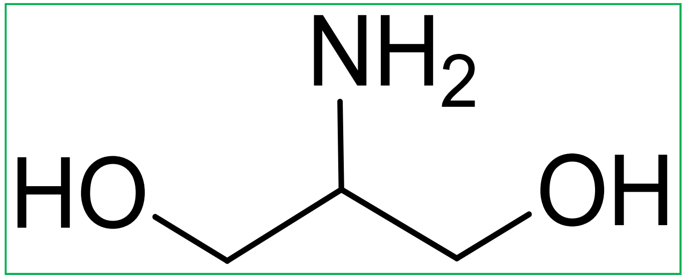
- ☞ Selection of starting building block
- ☞ Synthesis of derivatives: control of reaction pathways
- ☞ Innovative chemicals for rubber compounds
- ☞ Mechanical reinforcement: in brief
- ☞ Vulcanization: main subject

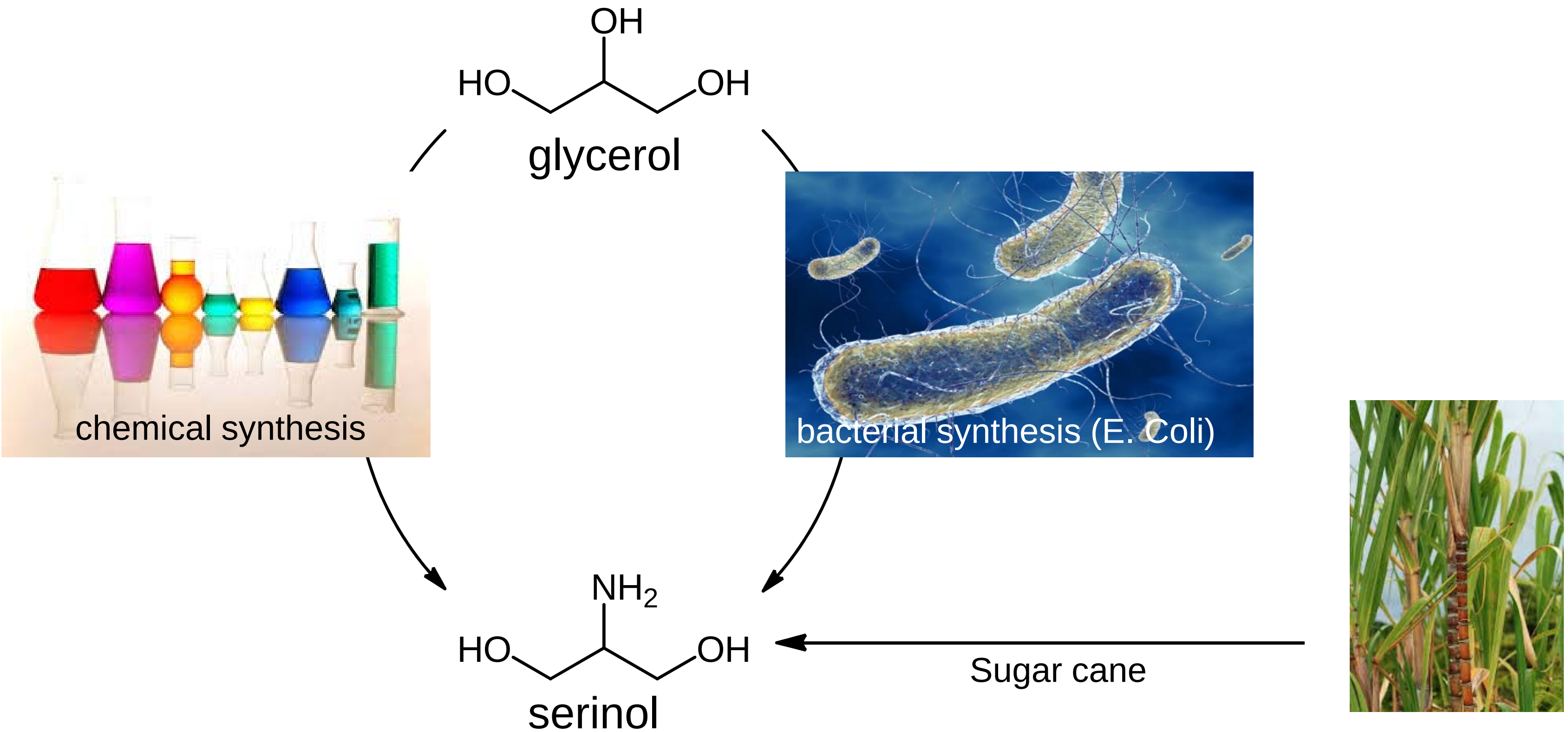
Selection of the building block: serinol



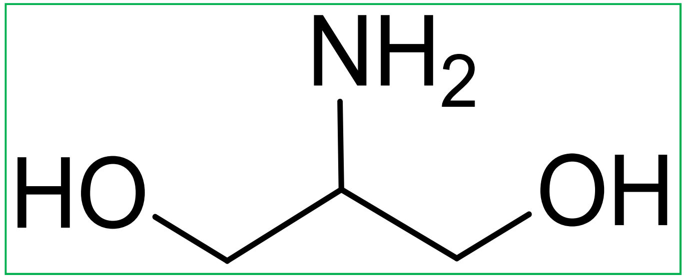
2-amino-1,3-propanediol

Selection of the building block: serinol



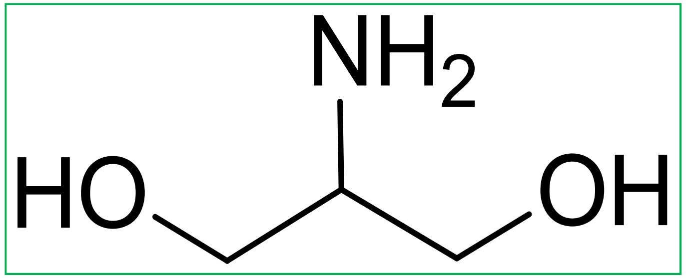


Why serinol for rubber compounds?



- Starting building block for many reaction pathways: many derivatives
- Chemoselectivity
- Interaction with polar fillers and polar surroundings
- Active role in vulcanization

Why serinol for rubber compounds?



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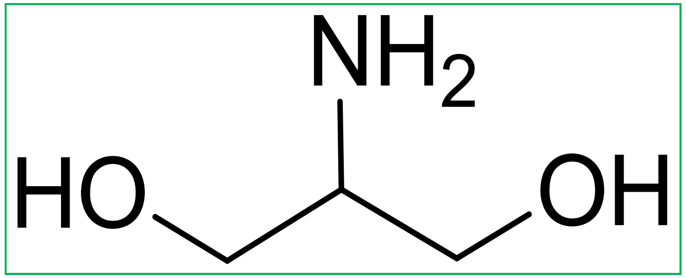


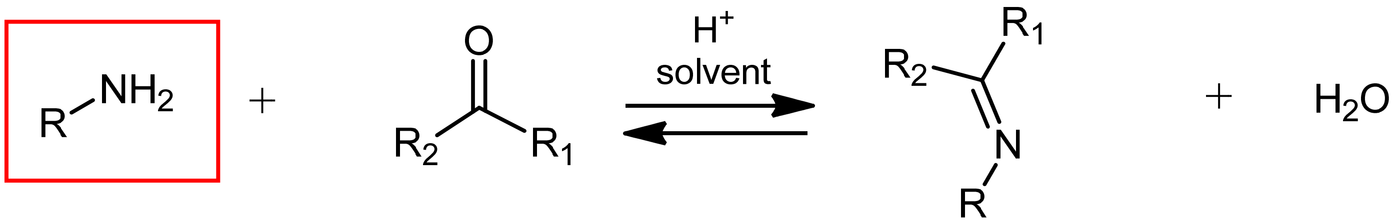
- Starting building block for many reaction pathways: many derivatives

- Chemoselectivity

↓

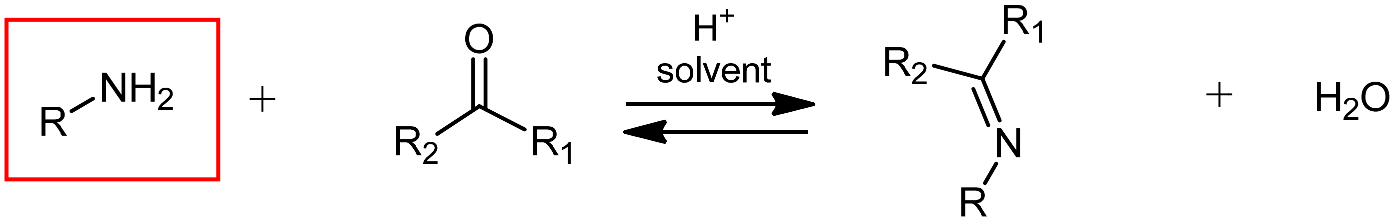
Reactions of the amino group with carbonyl compounds

Reactions of the primary amines with carbonyl compounds



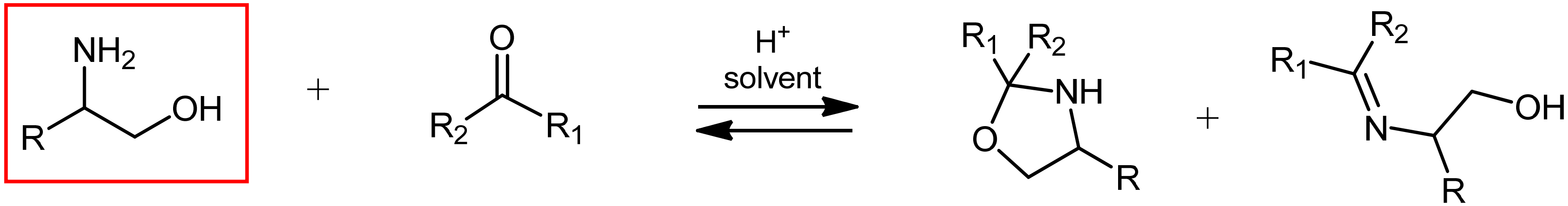
☞ Only imines are formed

Reactions of the primary amines with carbonyl compounds



☞ Only imines are formed

☞ With amino alcohols

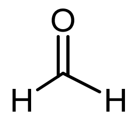


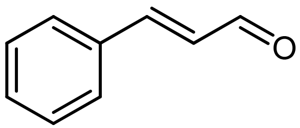
☞ Imines and Oxazolidines are formed

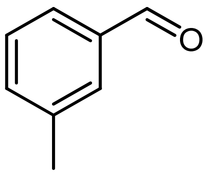
Reactions of serinol with carbonyl compounds

Carbonyl compounds

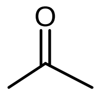
Aldehydes

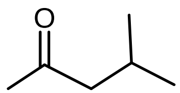

Formaldehyde

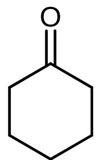

Cinnamaldehyde

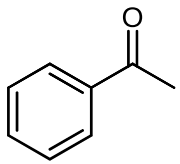

3-methylbenzaldehyde

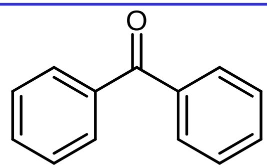
Ketones

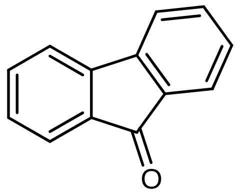

acetone

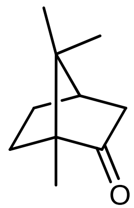

5-methylpentanone

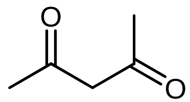

Cyclohexanone


Acetophenone


Benzophenone


Fluorenone

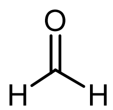
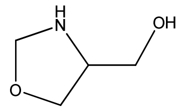
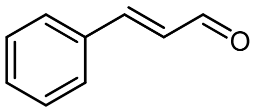
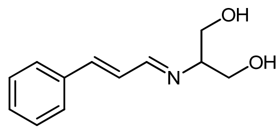
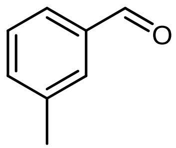
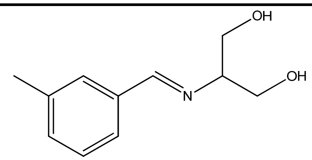

Camphor


2,4-pentandione

Neat reactions of serinol with aldehydes

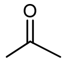
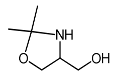
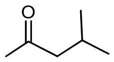
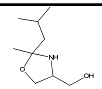
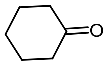
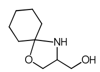
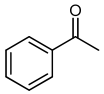
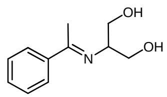
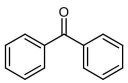
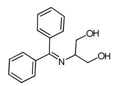
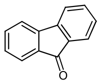
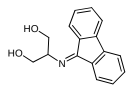
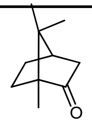
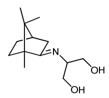
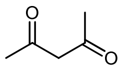
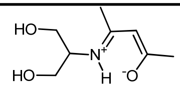
No solvent, no catalyst, T > melting point of carbonyl compound

Neat reactions of serinol with aldehydes

Carbonyl compound	Yield (%)	Product	Type
	56		Oxazolidine
	92		Imine
	98		imine

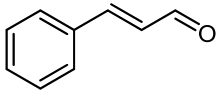
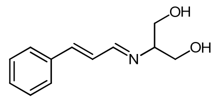
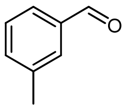
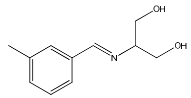
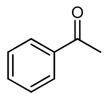
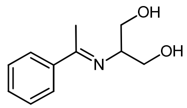
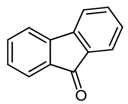
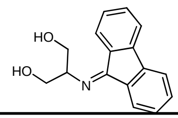
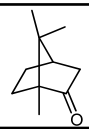
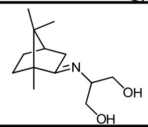
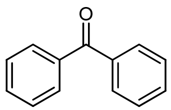
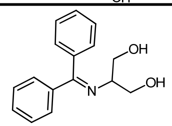
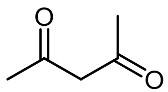
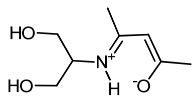
No solvent, no catalyst, T > melting point of carbonyl compound

Neat reactions of serinol with ketones

Carbonyl compound	Yield (%)	Product	Type
	90		Oxazolidine
	95		Oxazolidine
	90		Oxazolidine
	83		Imine
	75		Imine
	80		Imine
	70		Imine
	95		Imine

No solvent, no catalyst, T > melting point of carbonyl compound

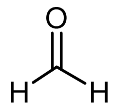
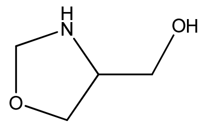
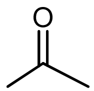
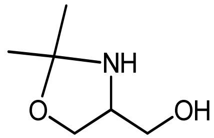
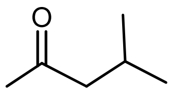
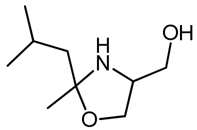
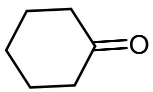
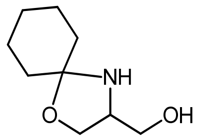
Imines from the reaction of serinol with carbonyl compounds

Carbonyl Compound	Product	Yield (%)
		92
		98
		83
		80
		70
		75
		95

Imines

☞ Aromatic and sterically hindered carbonyl compounds lead to Imines

Oxazolidines from the reaction of serinol with carbonyl compounds

Carbonyl Compound	Product	Yield (%)
		56
		90
		95
		90

Oxazolidines

☞ Aliphatic carbonyl compounds with low steric hindrance lead to oxazolidines

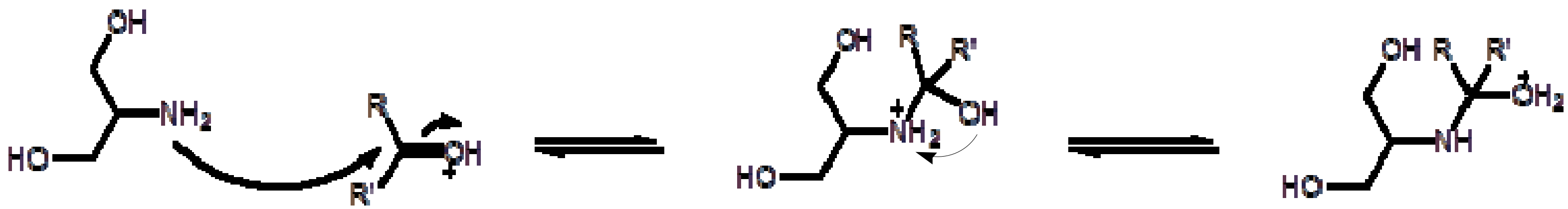
Reaction of serinol with carbonyl compounds. Mechanism

In the presence of acidic catalyst

I

Reaction of serinol with carbonyl compounds. Mechanism

In the presence of acidic catalyst

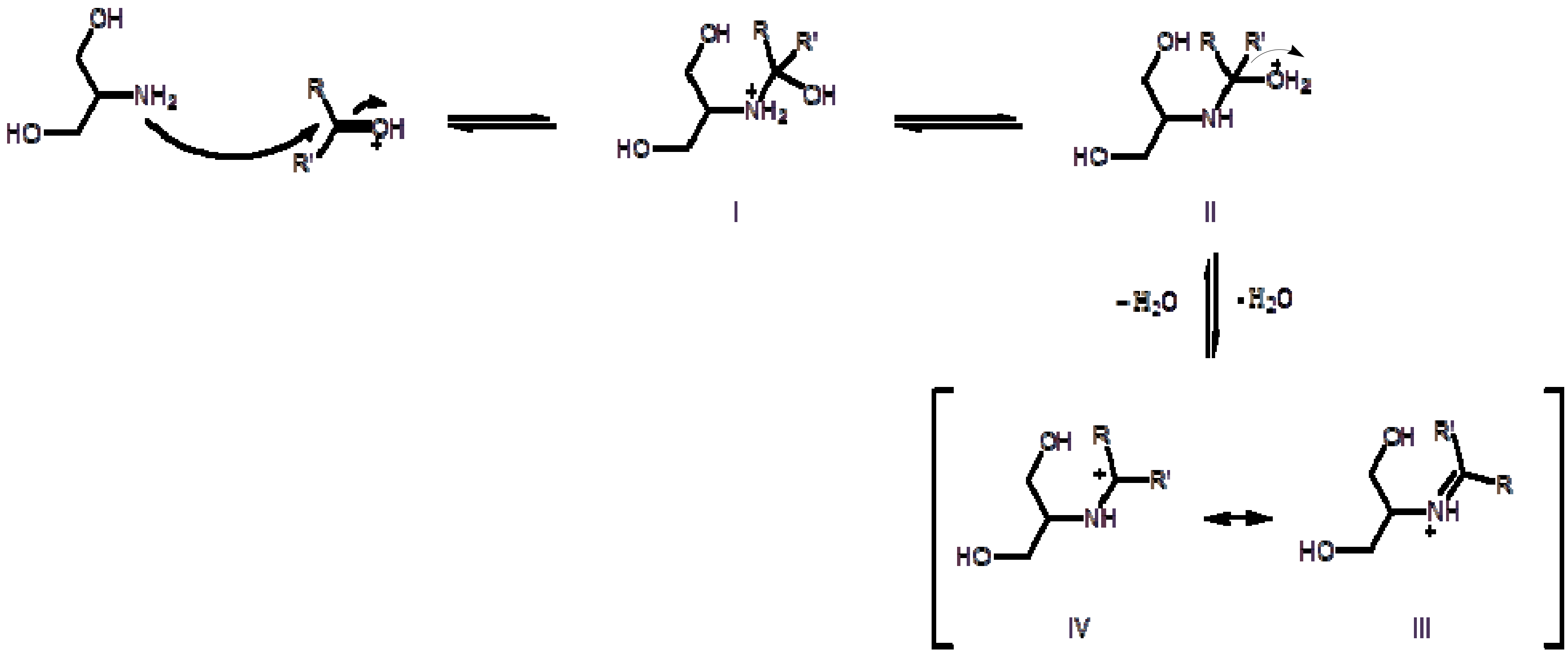


I

II

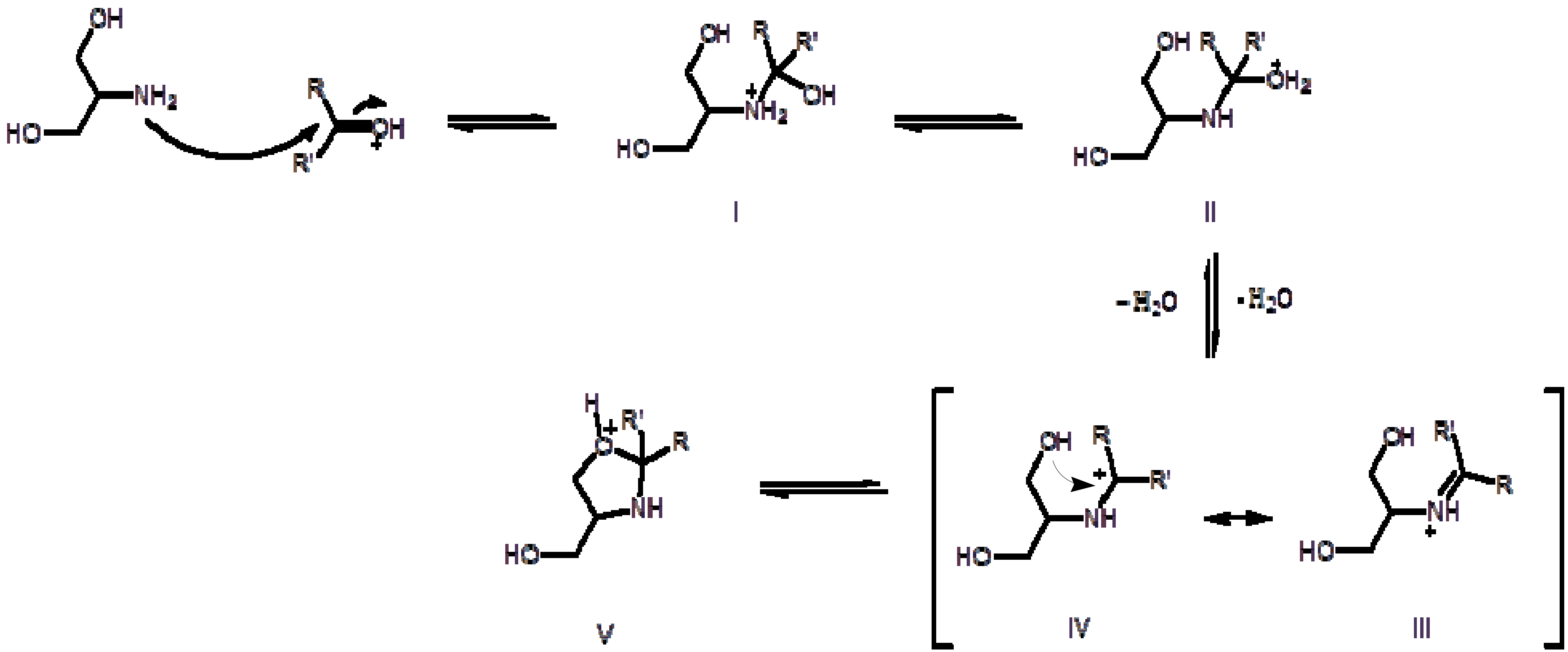
Reaction of serinol with carbonyl compounds. Mechanism

In the presence of acidic catalyst



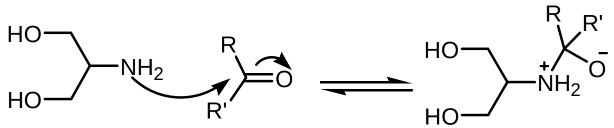
Reaction of serinol with carbonyl compounds. Mechanism

In the presence of acidic catalyst



Reaction of serinol with carbonyl compounds. Mechanism

Without acidic catalyst

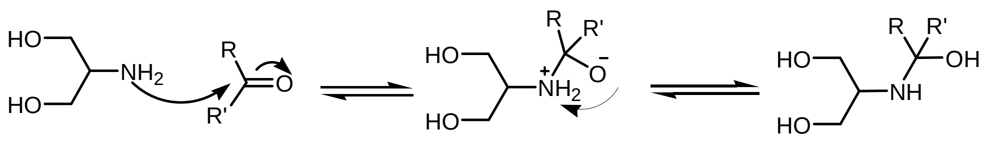


first molecule

VI

Reaction of serinol with carbonyl compounds. Mechanism

Without acidic catalyst



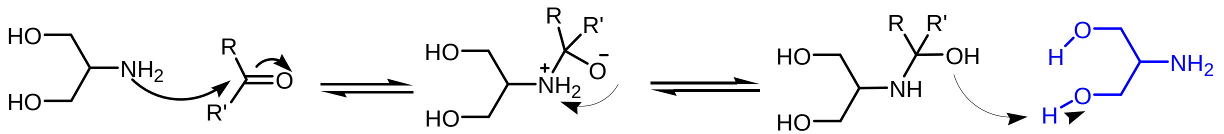
first molecule

VI

VII

Reaction of serinol with carbonyl compounds. Mechanism

Without acidic catalyst



first molecule

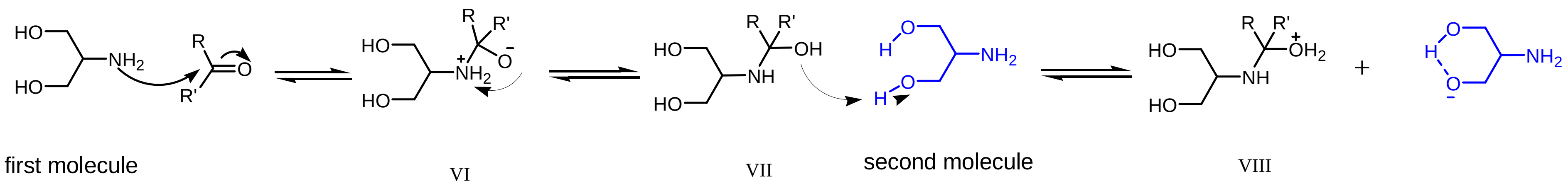
VI

VII

second molecule

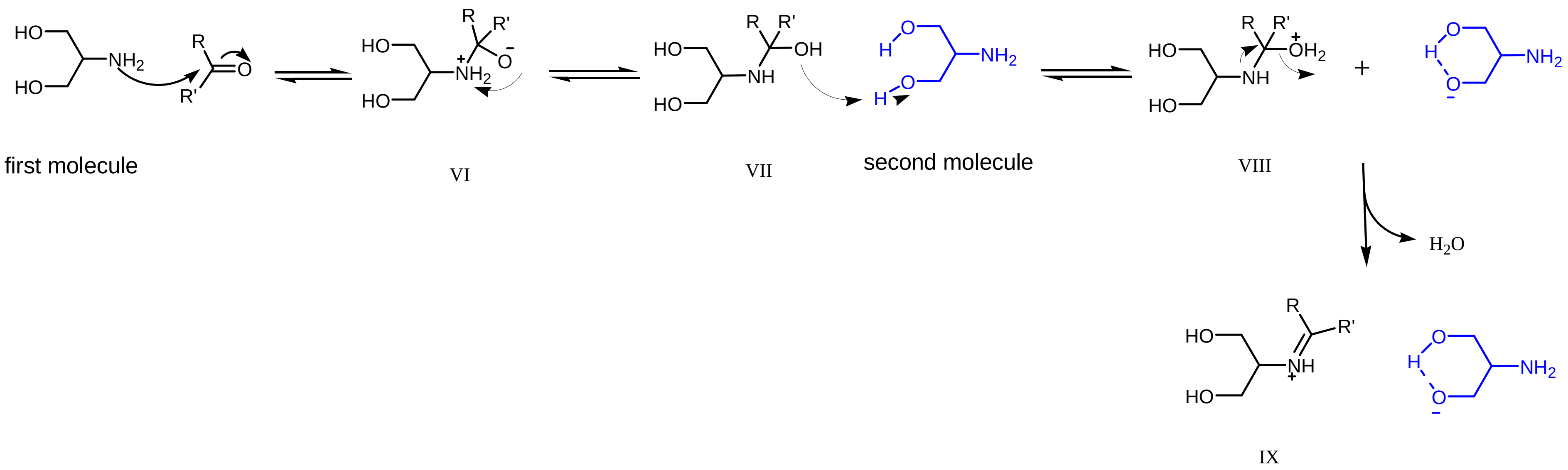
Reaction of serinol with carbonyl compounds. Mechanism

Without acidic catalyst



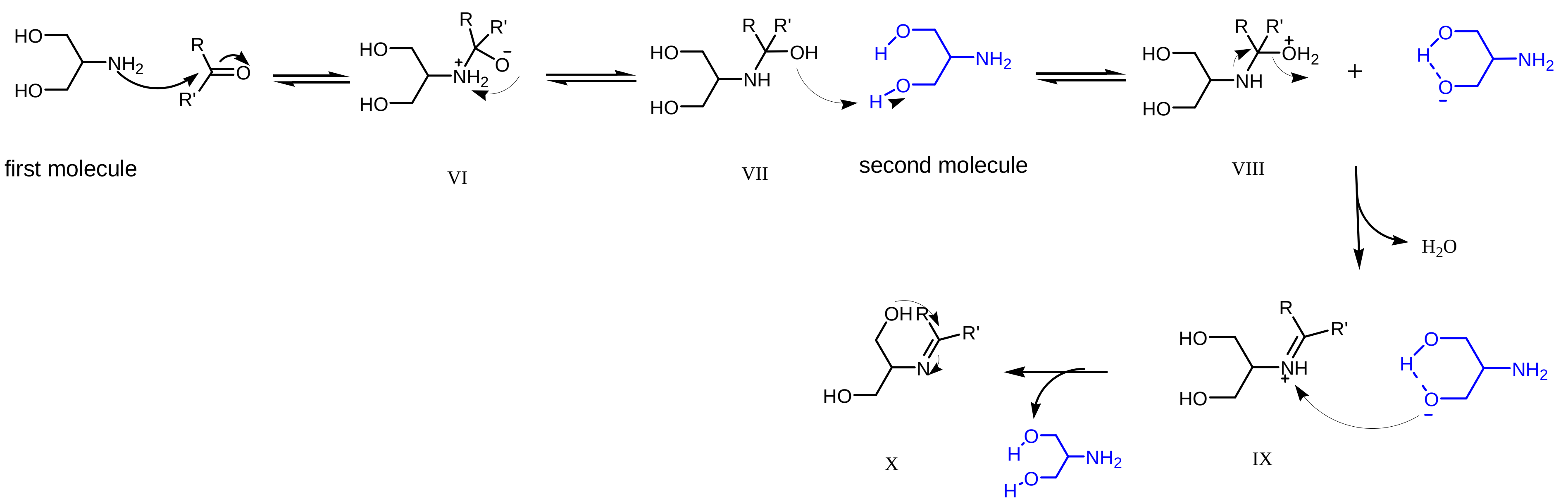
Reaction of serinol with carbonyl compounds. Mechanism

Without acidic catalyst



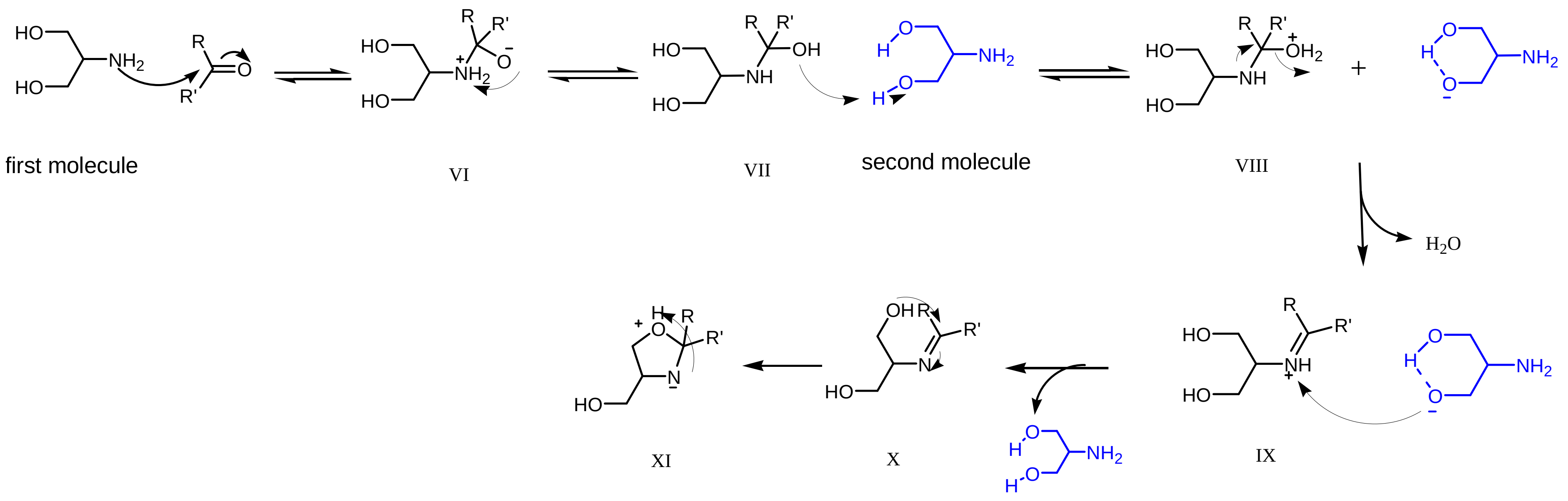
Reaction of serinol with carbonyl compounds. Mechanism

Without acidic catalyst



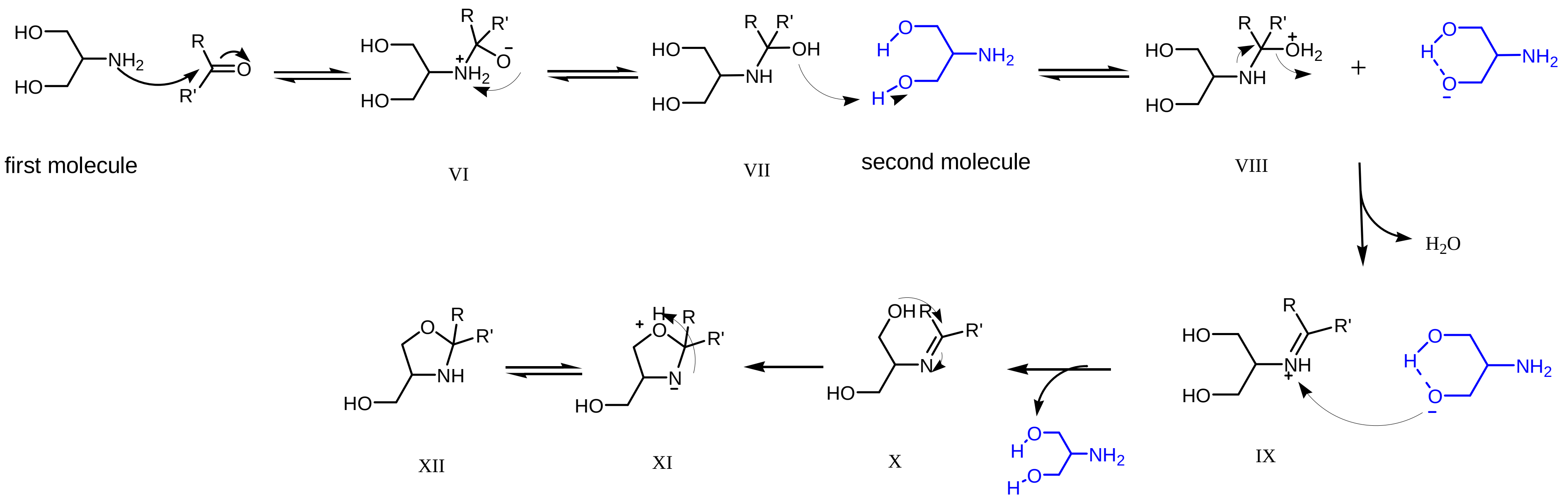
Reaction of serinol with carbonyl compounds. Mechanism

Without acidic catalyst



Reaction of serinol with carbonyl compounds. Mechanism

Without acidic catalyst

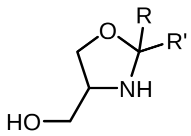


Reaction of serinol with carbonyl compounds. Mechanism

Without acidic catalyst

Without steric hindrance

and aromatic substituents

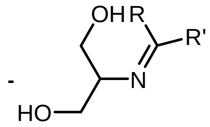


XII

Oxazolidines

With steric hindrance

and aromatic substituents

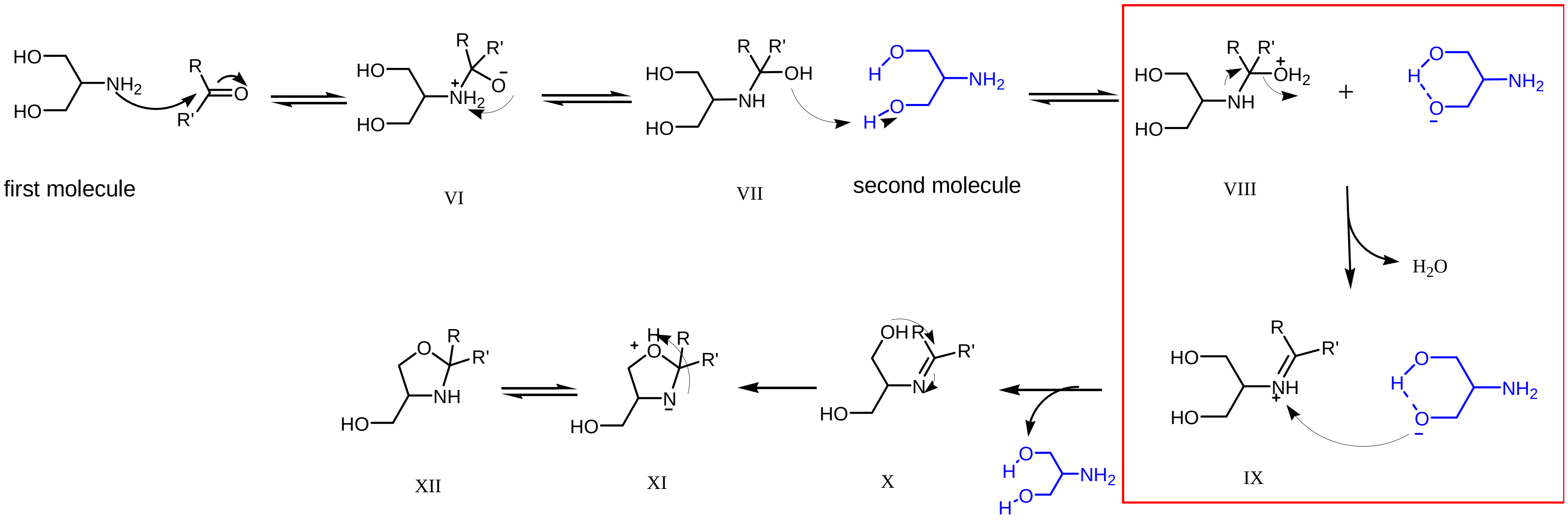


X

Imines

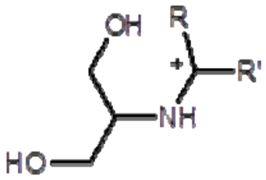
Reaction of serinol with carbonyl compounds. Mechanism

Without acidic catalyst



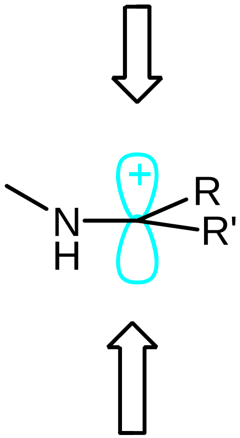
Reaction of serinol with carbonyl compounds. Key intermediates

In the presence of acidic catalyst



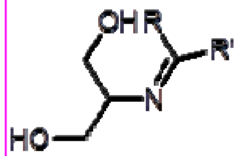
IV

Nucleophile

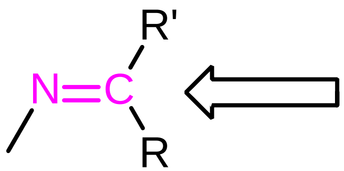


Nucleophile

Without acidic catalyst

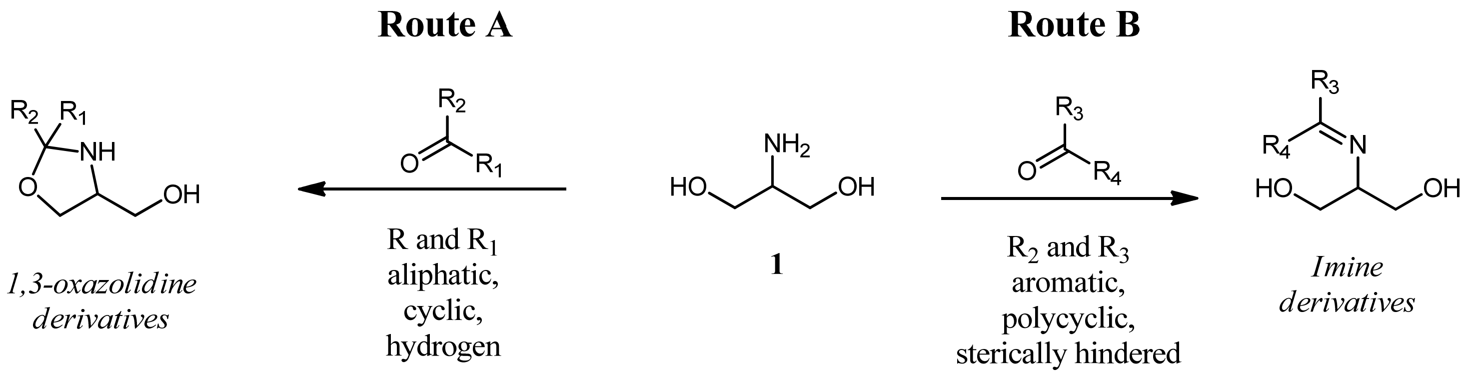


X

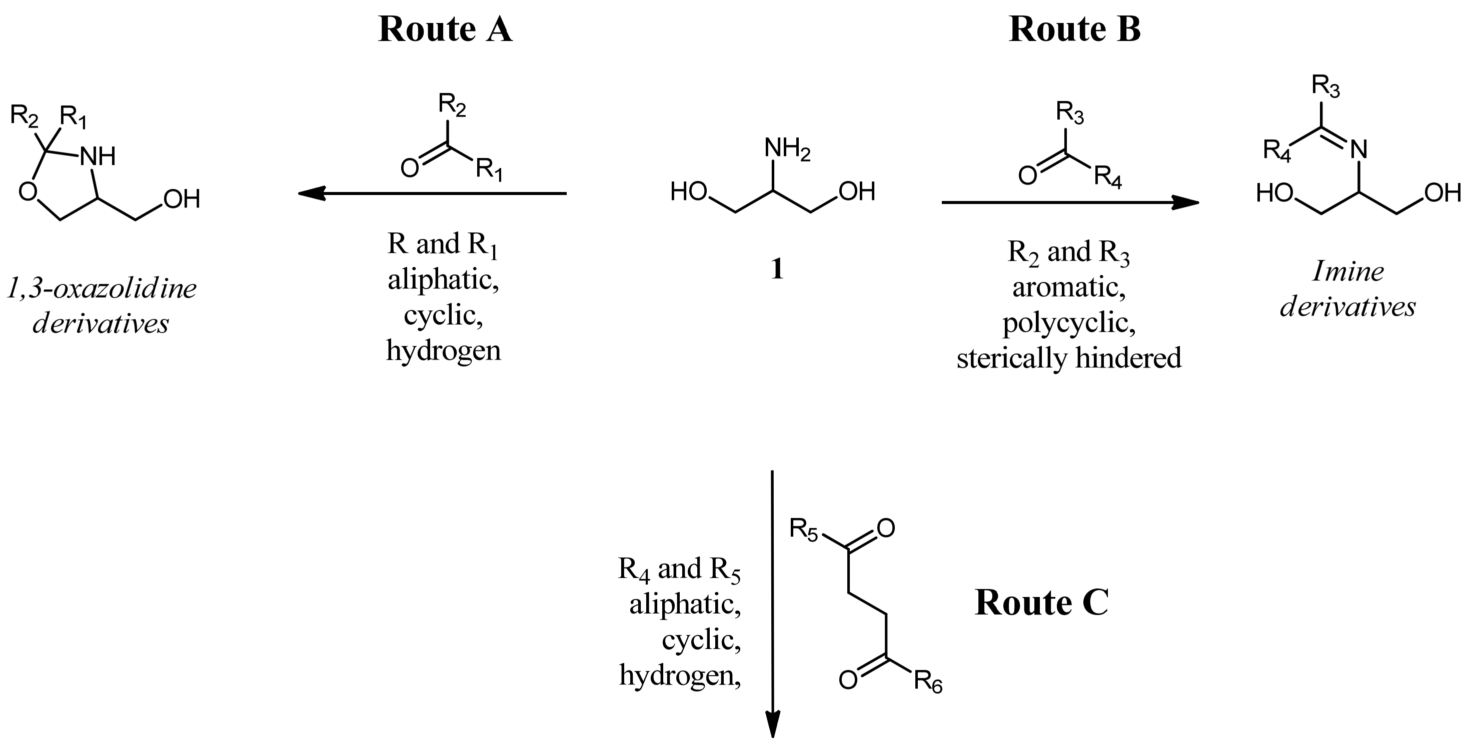


Nucleophile

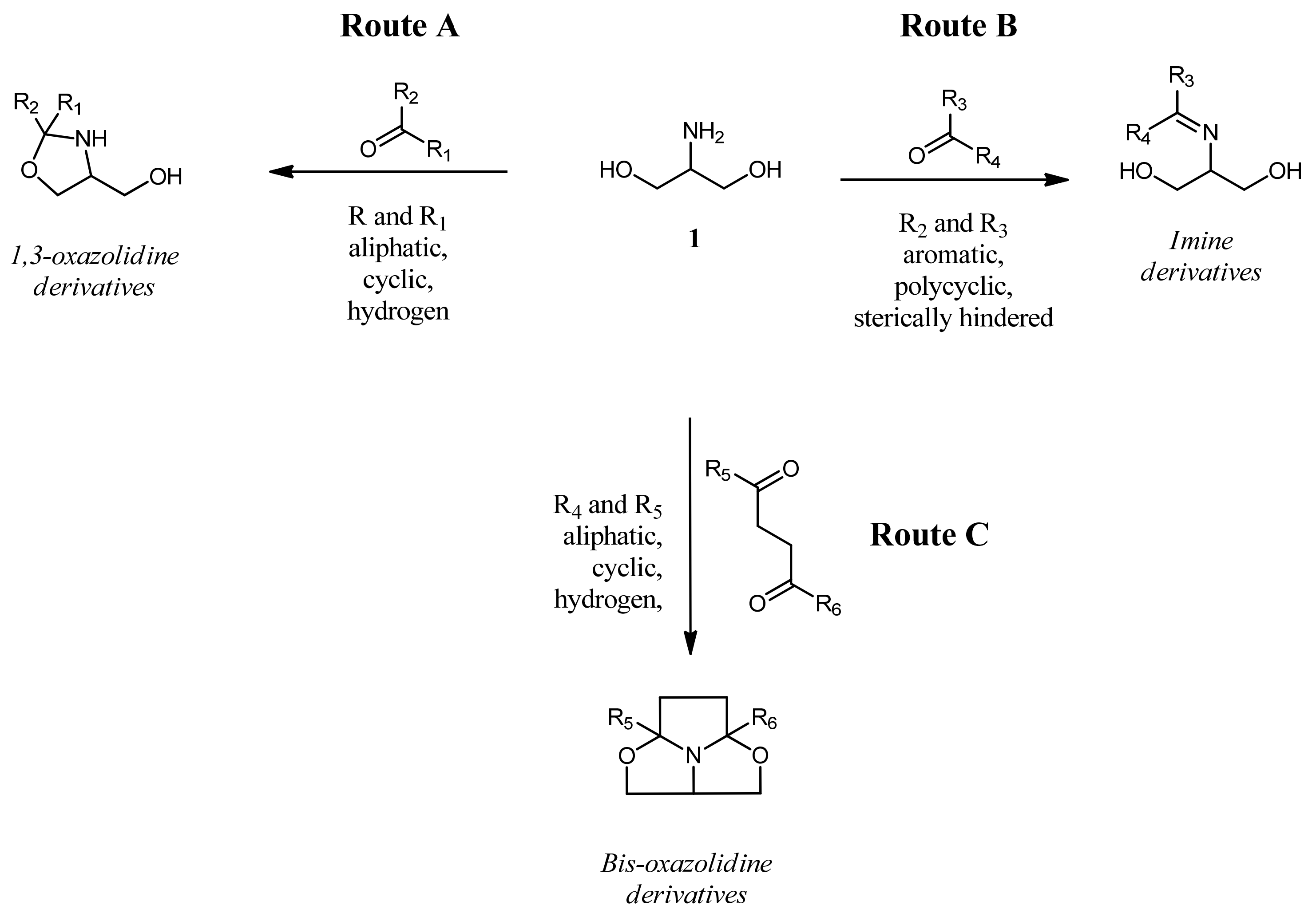
Control of synthetic pathways to serinol imines and oxazolidines



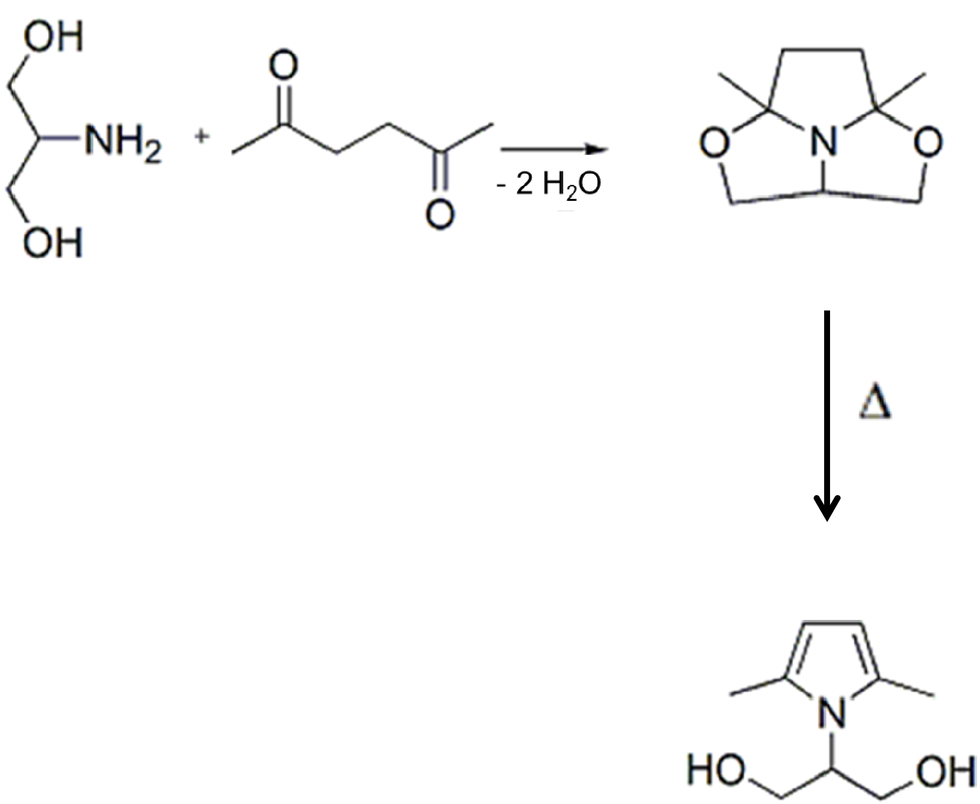
Control of synthetic pathways to serinol imines and oxazolidines



Control of synthetic pathways to serinol imines and oxazolidines



Reaction of serinol with dicarbonyl compound

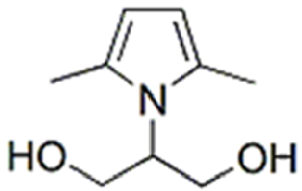


Serinol and serinol derivatives

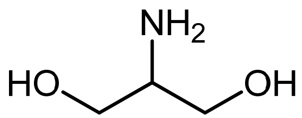
for rubber compounds

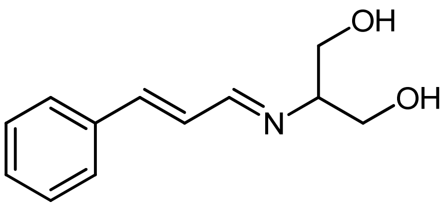
Serinol and serinol derivatives for rubber compounds

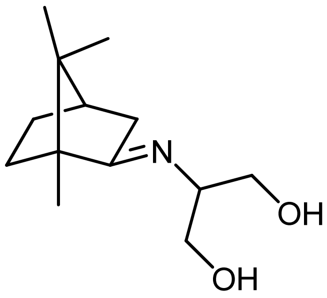
Mechanical properties

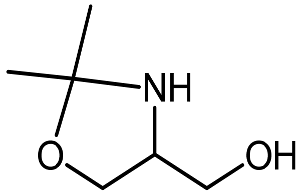


Vulcanization

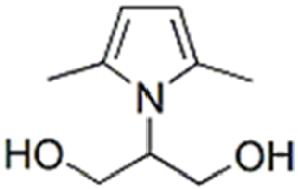








Mechanical properties



Functionalization of sp^2 carbon allotropes

sp^2 carbon allotropes

+

SP

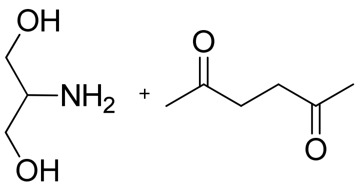
↓ thermal or mechanical energy

Functionalized sp^2 carbon allotropes

M. Galimberti, V. Barbera, R. Sebastiano, A. Citterio, G. Leonardi, A.M. Valerio WO 2016 050887 A1

M. Galimberti, V. Barbera, S. Guerra, A. Bernardi, Rubber Chemistry and Technology: 2017, 90(2) 285-307

Domino reaction for the functionalization of sp^2 carbon allotropes



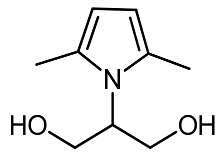
Carbon allotrope

CB

HSAG

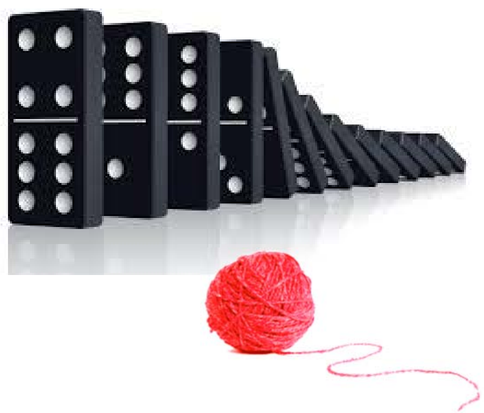
CNT

Paal – Knorr reaction to SP



Carbocatalyzed Oxidation of SP

Diels-Alder reaction



M. Galimberti, V. Barbera, S. Guerra, A. Bernardi, Rubber Chemistry and Technology: 2017, 90(2) 285-307

CB-SP in CB/Silica based composite

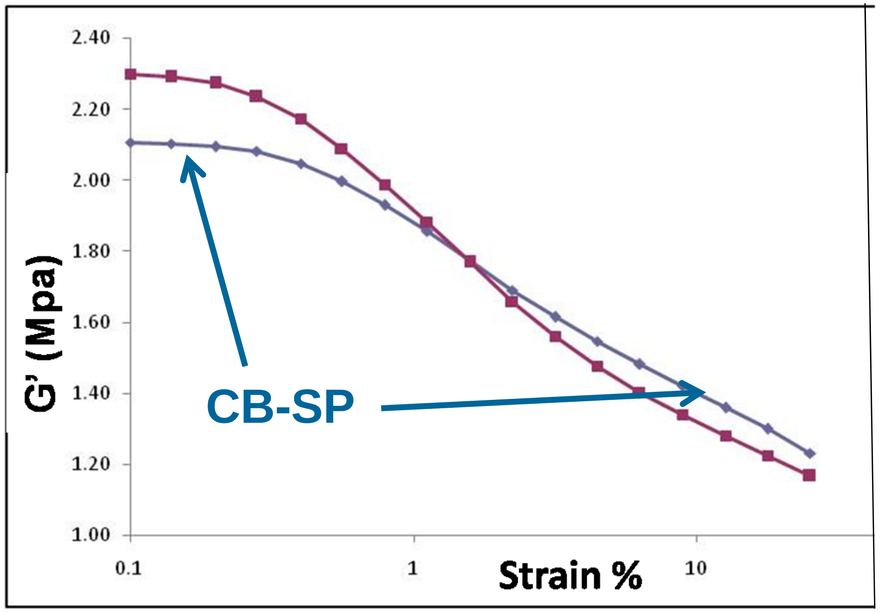
Ingredient	With CB	With CB-SP
CB N326	25	0
CB N326-SP	0	27
CB326	0	25
SP	0	2

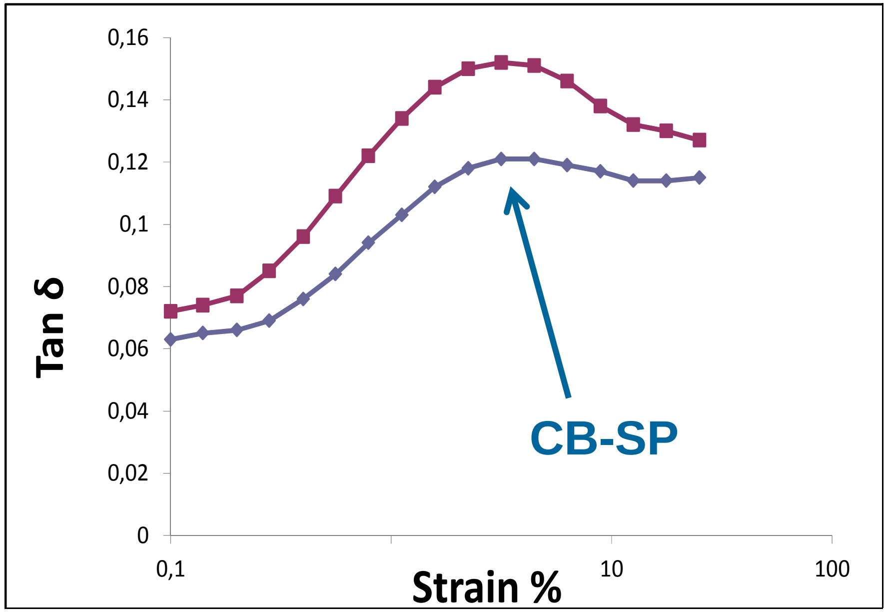
IR 50, BR 50, Silica 50,

Silane TESPT 2, Stearic acid 2, ZnO 2.5, 6PPD 2,

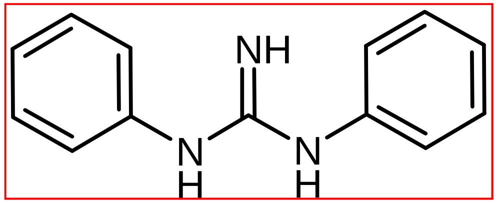
Sulphur 1.5, TBBS 1.8

CB-SP in CB/Silica based composite

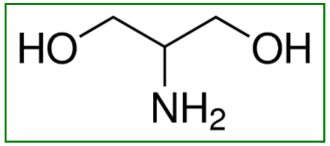




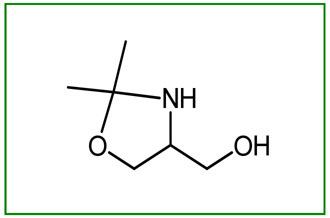
Serinol and serinol derivatives for rubber compounds



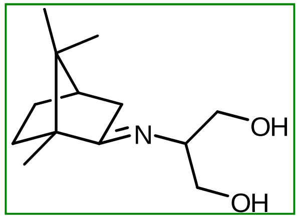
DPG



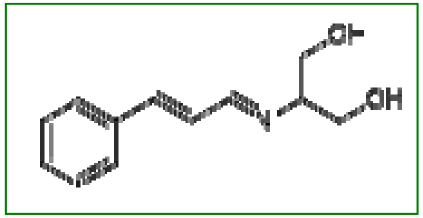
Serinol



Serinol acetone oxazolidine



Serinol camphor imine

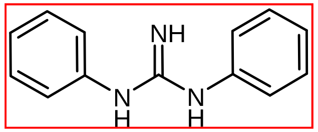
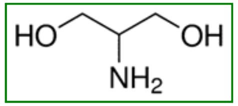
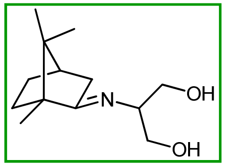
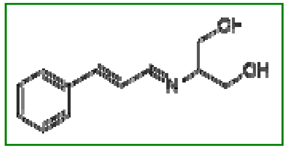


Serinol cinnamaldehyde imine

M. Galimberti, R. Sebastiano, V. Barbera, V. Cipolletti, G. Leonardi, S. Sun, L. Rossiello WO 2017/115253 A1

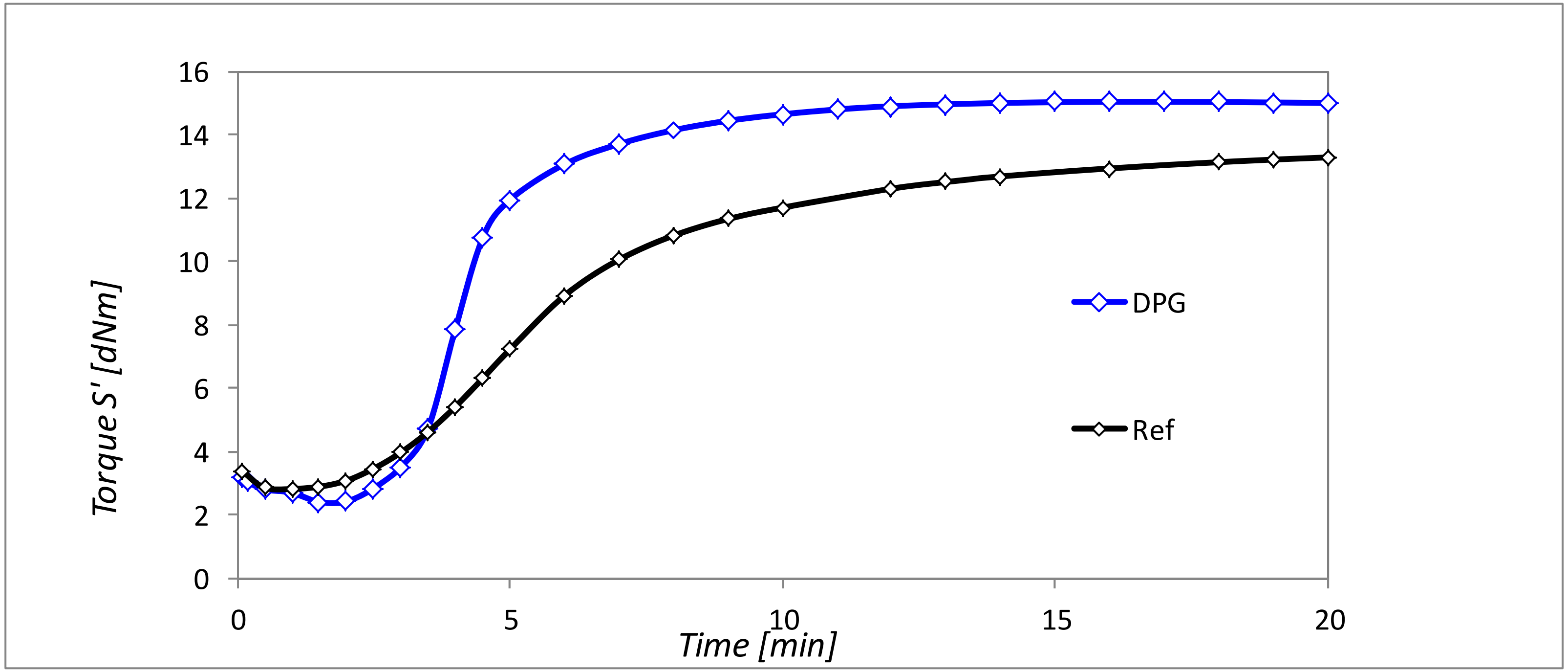
Serinol and serinol derivatives as secondary accelerators in silica based compounds

Ingredient	phr
S-SBR	96.3
NR	15
BR	15
Silica	65
Silane TESPT Si69	5.6
Oil MES	10
Stearic Acid	2
ZnO	2.5
6PPD	2
Sulphur	1.8
TBBS	1.2
Secondary accelerator	X

Secondary accelerator	X phr
	2.4
or 	0.83
or 	2.04
or 	1.87

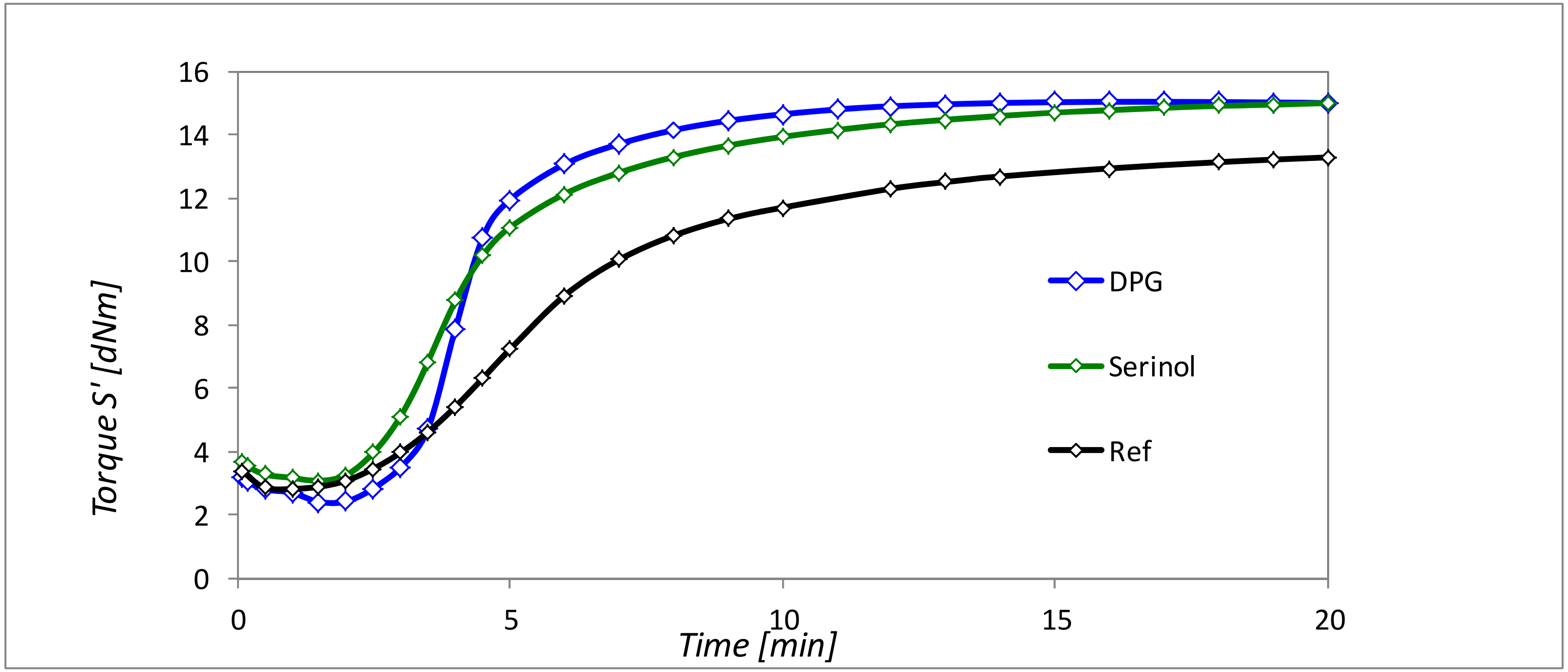
Secondary accelerators were used in equal molar amount

Curing at 170°C



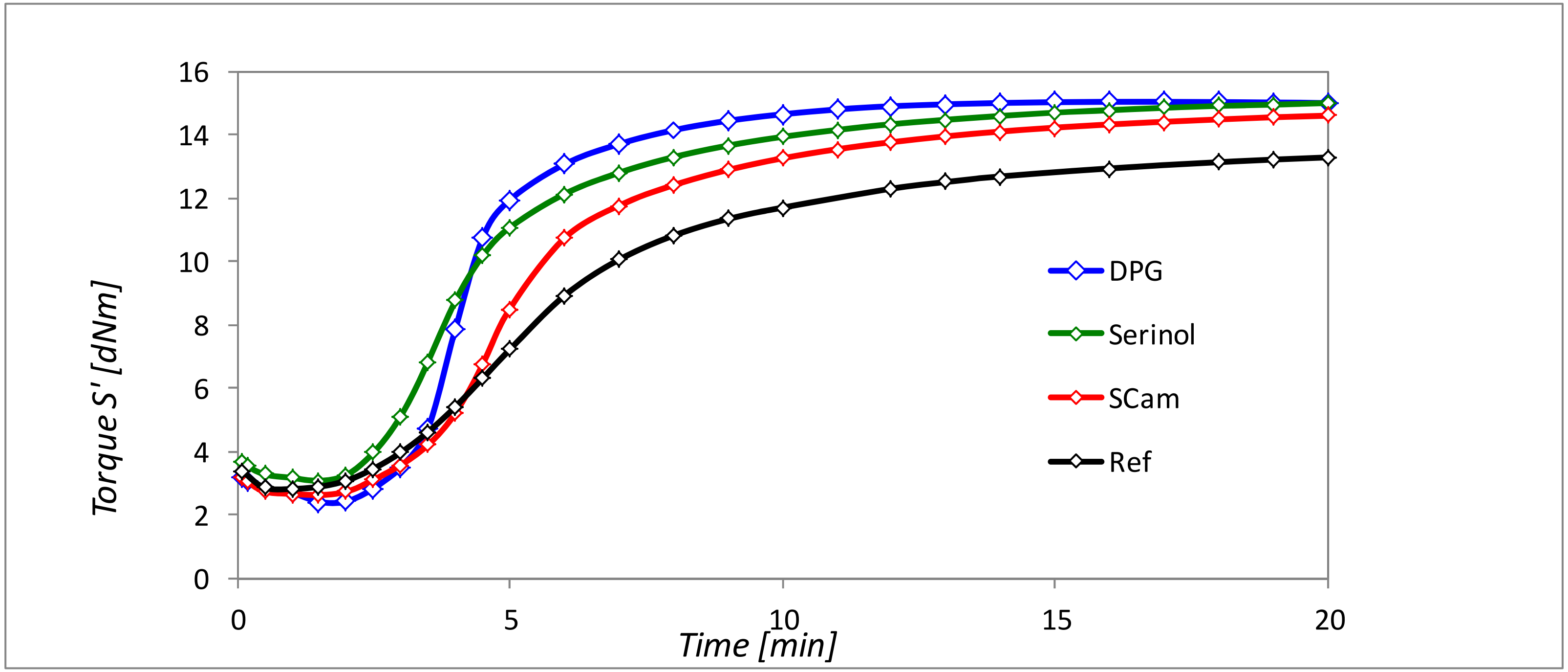
Secondary accelerator		=	DPG
Parameter			
M_L	[dNm]	2.8	2.3
M_H	[dNm]	13.3	15.1
t_{s1}	[min]	2.8	2.9
t_{90}	[min]	11.5	7.1

Curing at 170°C



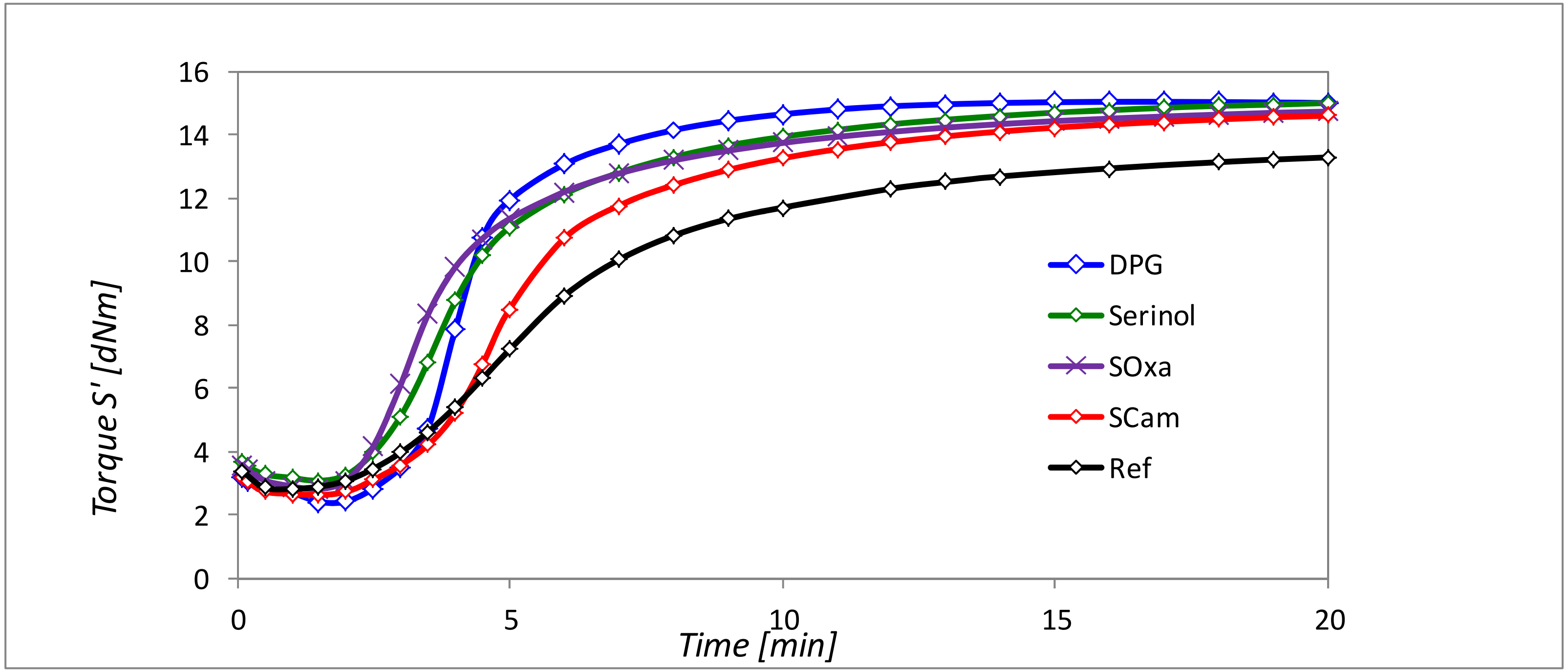
Secondary accelerator		=	DPG	Serinol
Parameter				
M_L	[dNm]	2.8	2.3	3.1
M_H	[dNm]	13.3	15.1	15.0
t_{s1}	[min]	2.8	2.9	2.6
t_{90}	[min]	11.5	7.1	9.5

Curing at 170°C



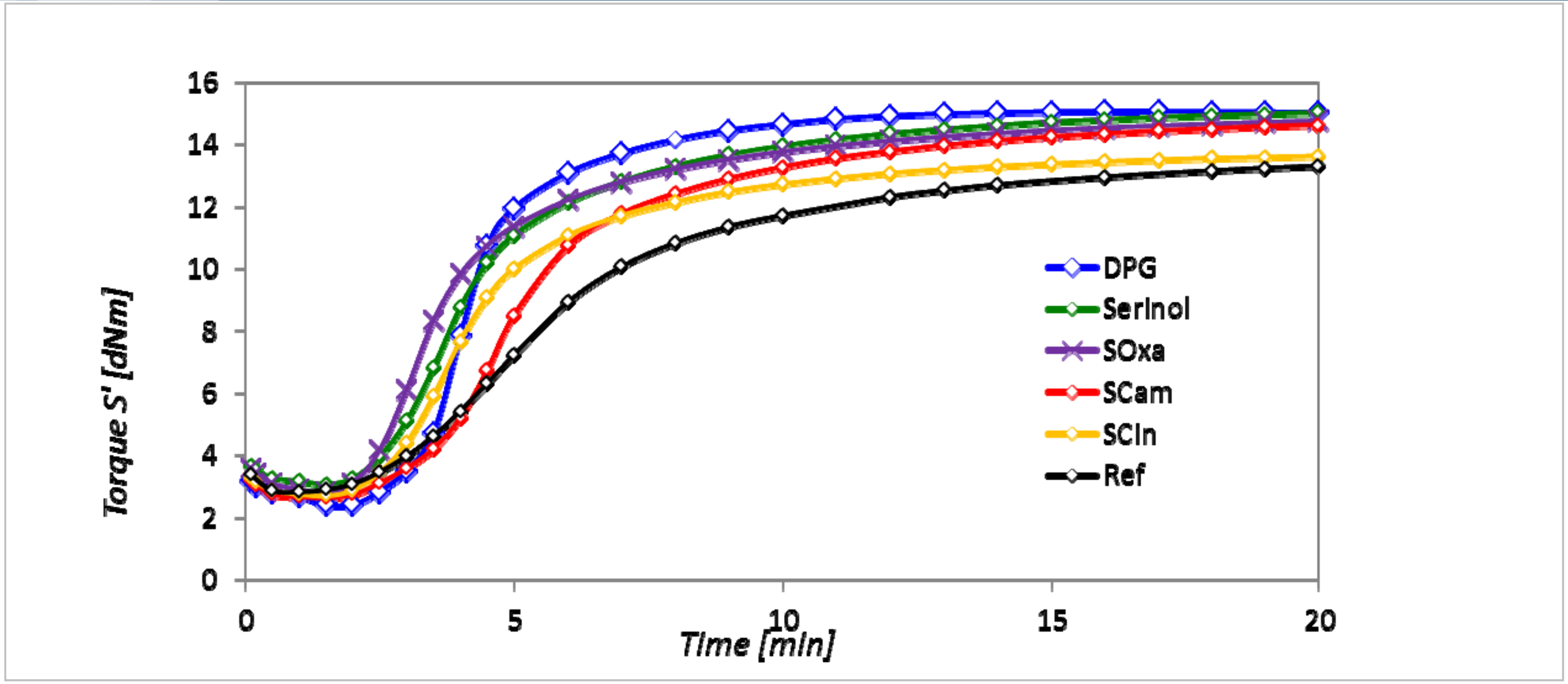
Secondary accelerator		=	DPG	Serinol	SCam
Parameter					
M_L	[dNm]	2.8	2.3	3.1	2.6
M_H	[dNm]	13.3	15.1	15.0	14.6
t_{s1}	[min]	2.8	2.9	2.6	3.0
t_{90}	[min]	11.5	7.1	9.5	10.5

Curing at 170°C



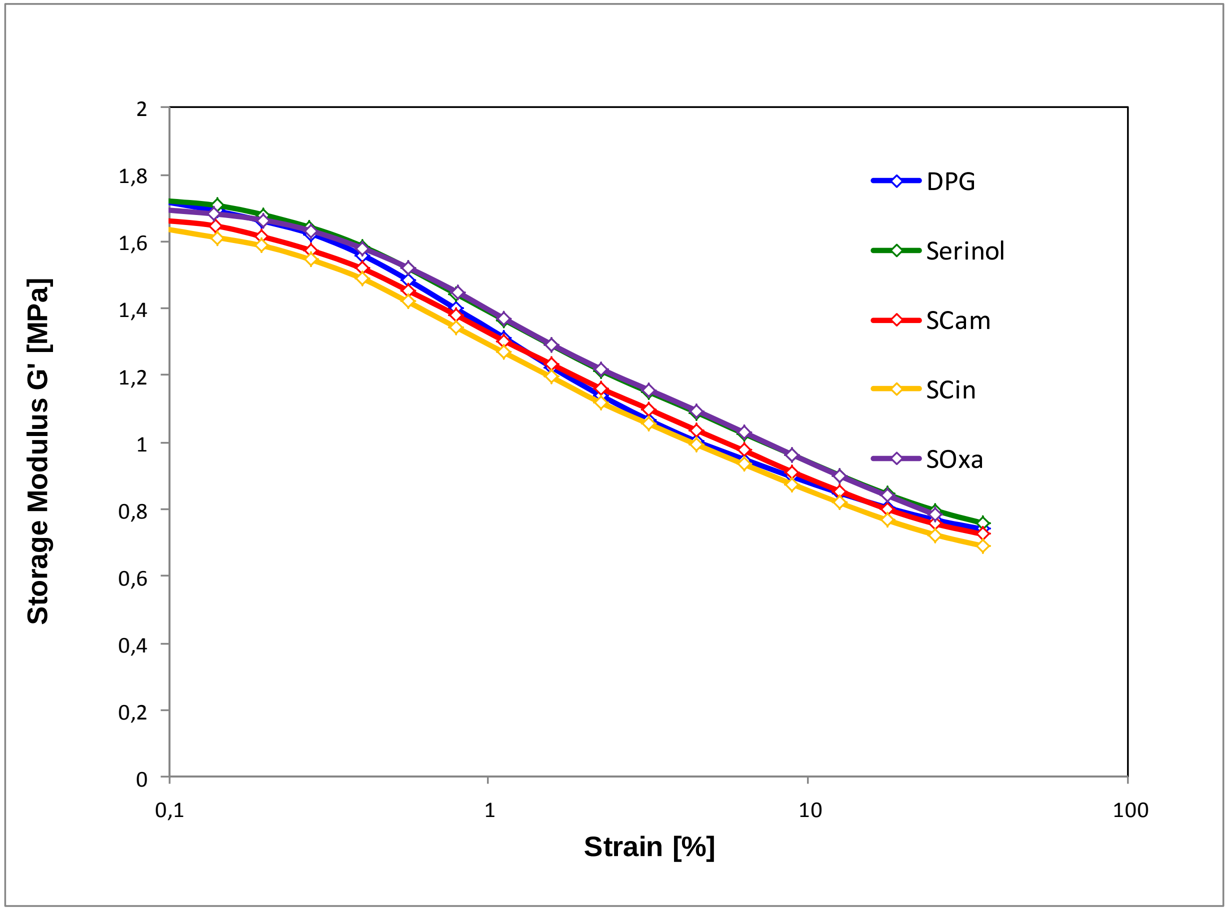
Secondary accelerator		=	DPG	Serinol	SCam	SOxa
Parameter						
M_L	[dNm]	2.8	2.3	3.1	2.6	2.8
M_H	[dNm]	13.3	15.1	15.0	14.6	14.8
t_{s1}	[min]	2.8	2.9	2.6	3.0	2.4
t_{90}	[min]	11.5	7.1	9.5	10.5	9.2

Curing at 170°C



Secondary accelerator		=	DPG	Serinol	SCam	SCin	SOxa
Parameter							
M_L	[dNm]	2.8	2.3	3.1	2.6	2.7	2.8
M_H	[dNm]	13.3	15.1	15.0	14.6	13.6	14.8
t_{s1}	[min]	2.8	2.9	2.6	3.0	2.7	2.4
t_{90}	[min]	11.5	7.1	9.5	10.5	9.2	9.2

Strain sweep at 170°C



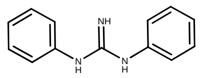
Scorch time at 130°C

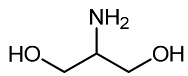
Secondary accelerator		=	DPG	Serinol	SCam	SOxa	SCin
Parameter							
M_L	dNm	7.1	6.1	7.0	6.5	6.6	6.1
t_{s5} [a]	min	46.4	28.9	25.7	37.3	20.6	27.0

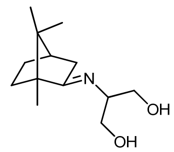
[a]Scorch time t_{s5}: = time needed to have an increase of torque of 5 dNm

Solvent extraction of silica / secondary accelerator masterbatches

Silica based masterbatch (1 : 1) with







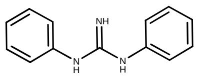
2 h
Boiling hexane

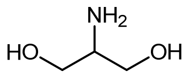
2 h
Boiling hexane

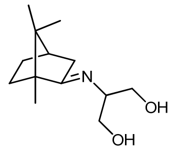
2 h
Boiling hexane

Solvent extraction of silica / secondary accelerator masterbatches

Silica based masterbatch (1 : 1) with





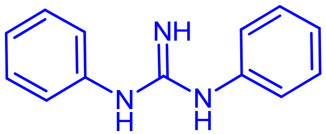


2 h
Boiling hexane

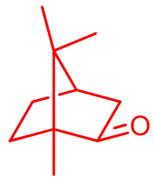
2 h
Boiling hexane

2 h
Boiling hexane

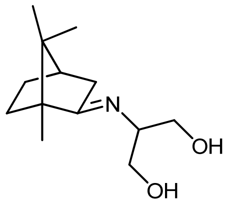
Extracted substance



NONE



Thermal treatment of silica / SCam masterbatch



+

SiO_2

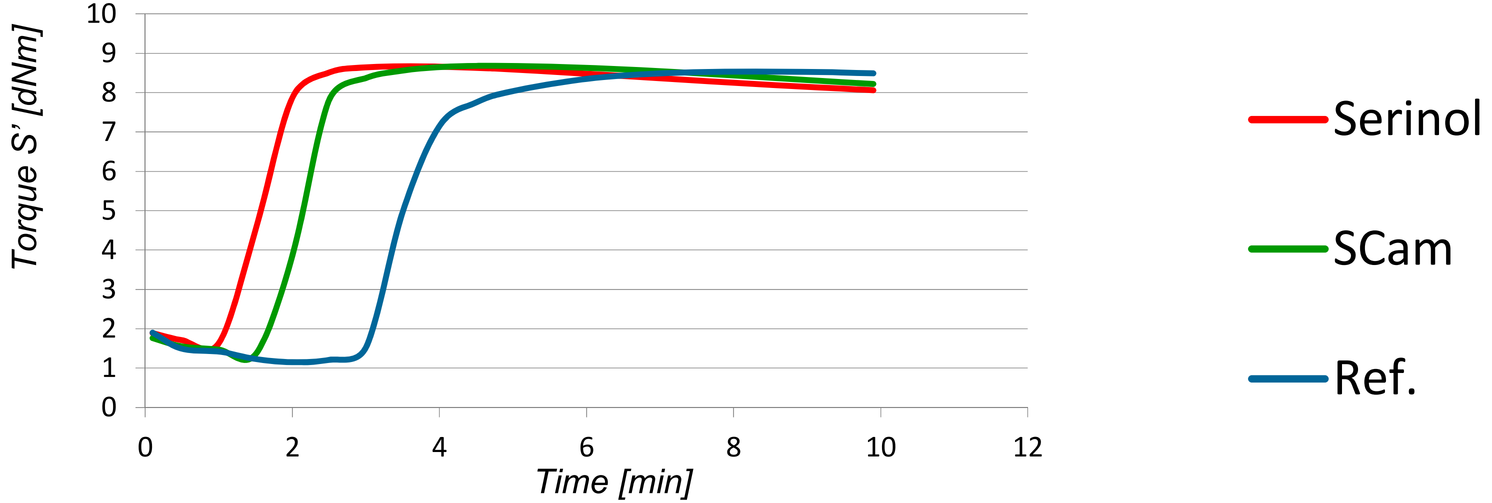
1 : 1

- r.t.,14 days → No weight loss
- 150°C, 2 h → weight loss → Camphor (80% extracted)

Serinol and serinol derivatives as secondary accelerators in NR based compounds

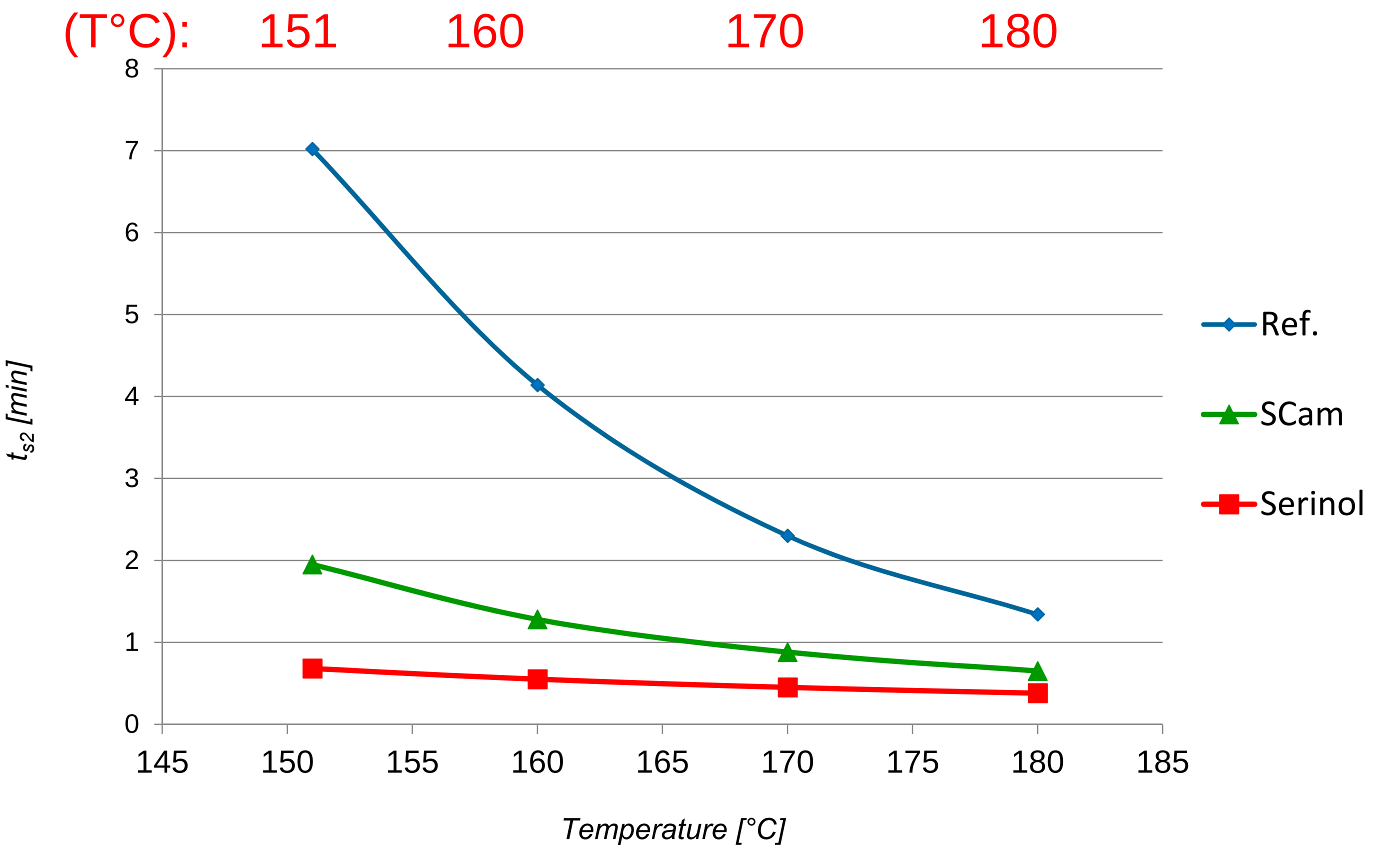
Ingredient	Composite		
	phr	phr	phr
NR	100	100	100
Stearic acid	2	2	2
ZnO	5	5	5
Sulphur	2	2	2
CBS	1.5	1.5	1.5
Serinol	-	0.83	-
Scam	-	-	2.04

Curing at 170°C

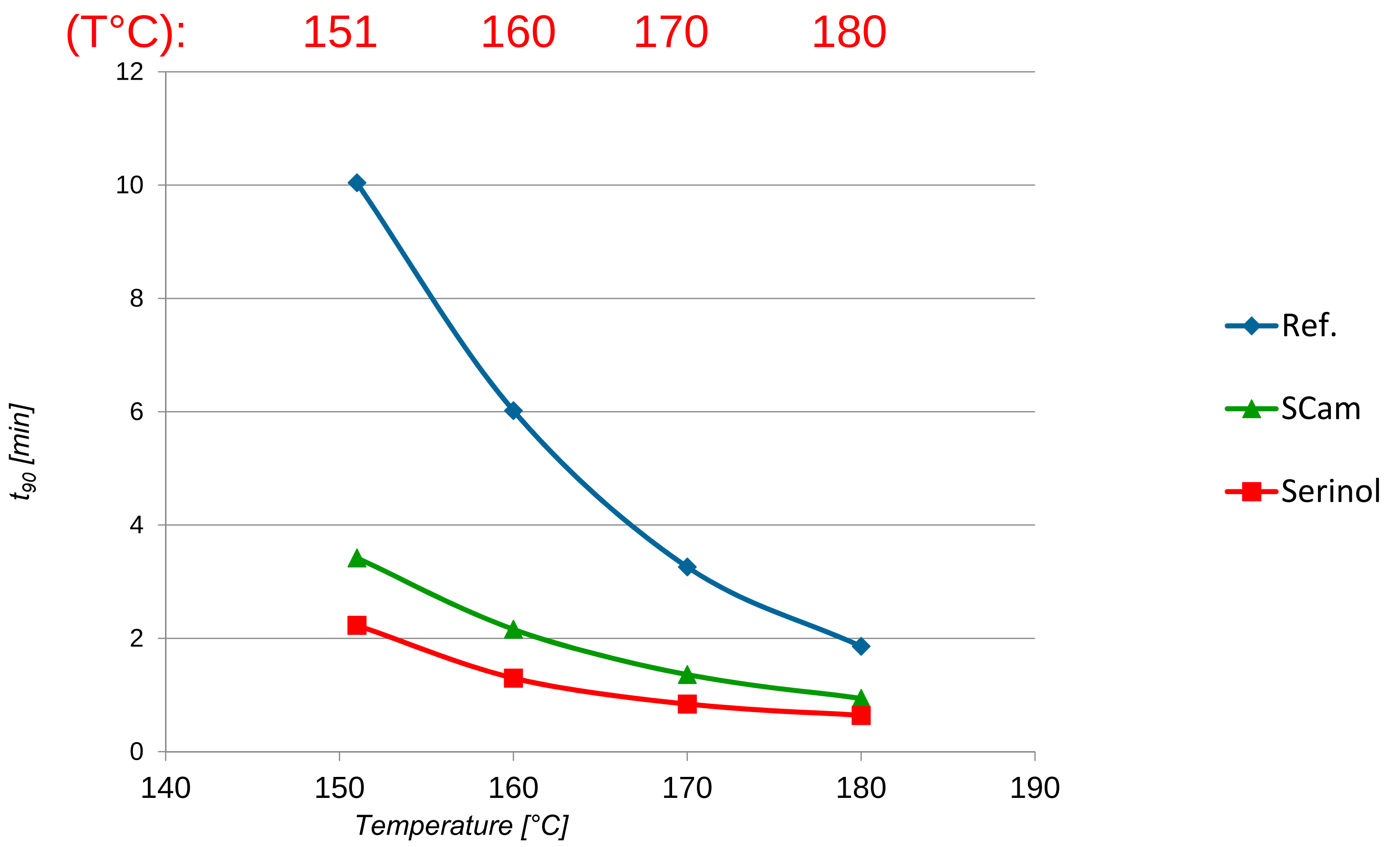


Secondary accelerator		=	Serinol	SCam
Parameter				
M_L	[dNm]	1.1	1.6	1.3
M_H	[dNm]	8.5	8.7	8.7
t_{s1}	[min]	2.1	2.6	2.3
t_{90}	[min]	4.6	2.0	2.6

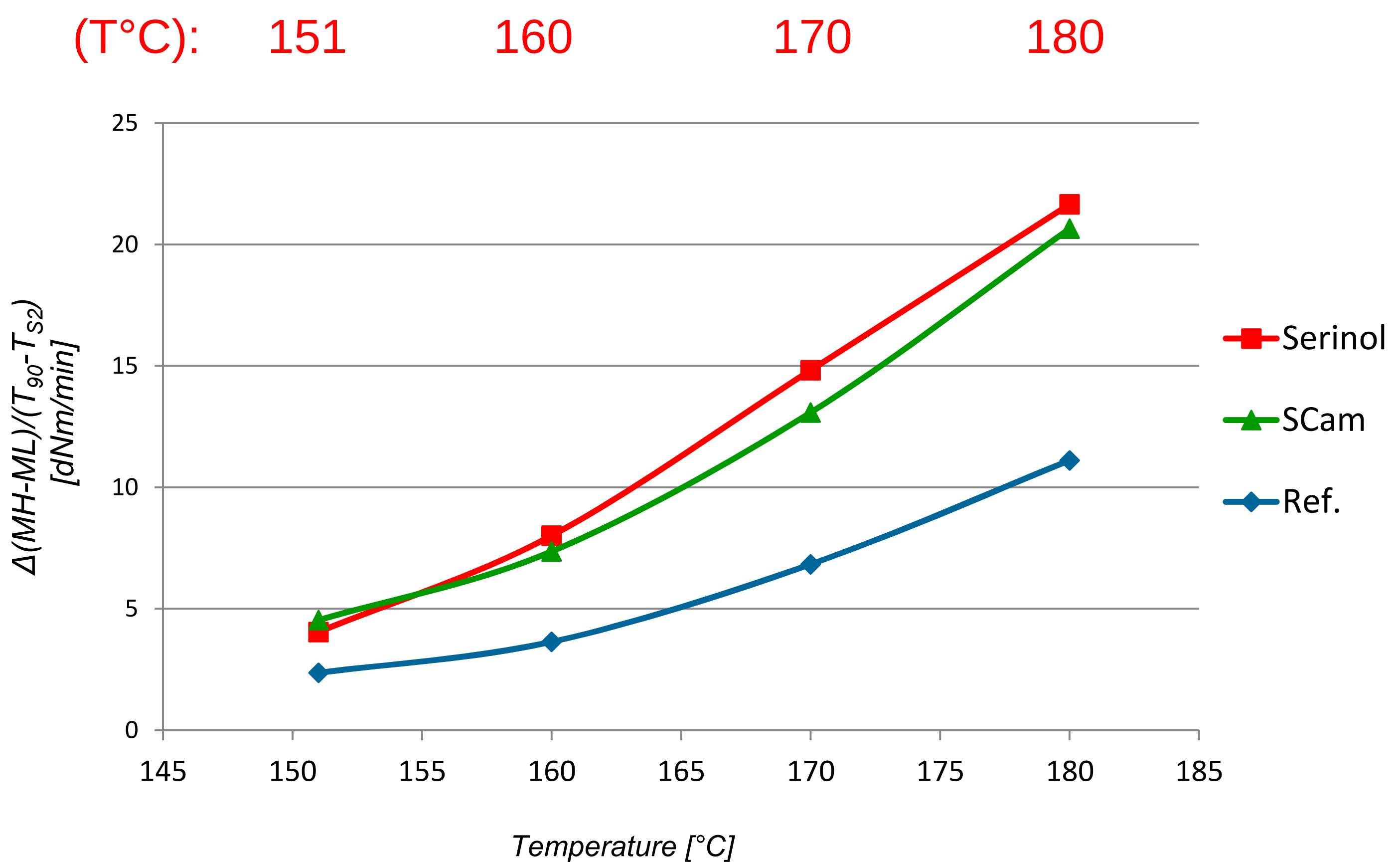
t_{s2} vs curing Temperature



t_{90} vs curing Temperature

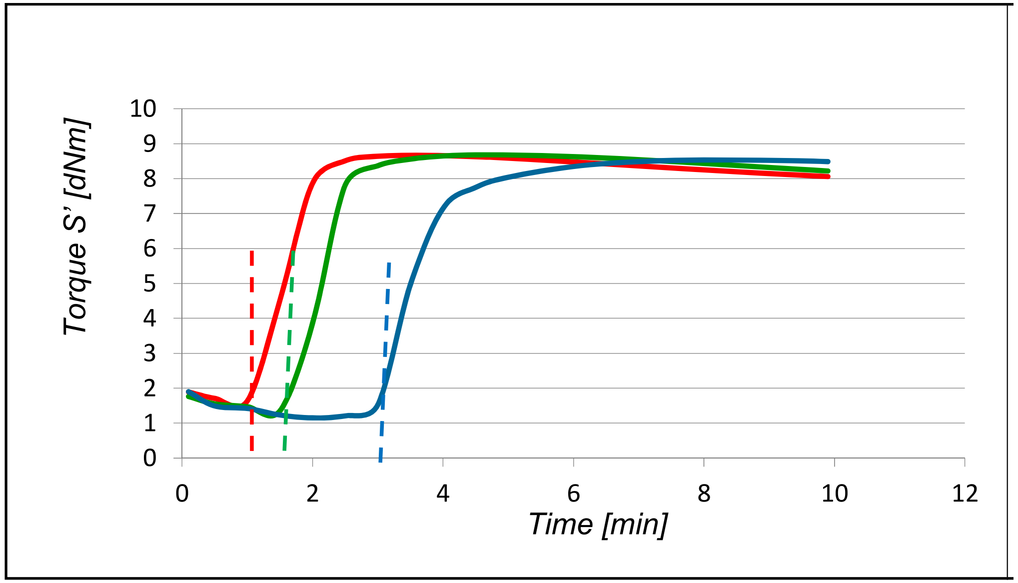


Vulcanization rate vs Temperature



Kinetics of vulcanization

Induction and crosslinking

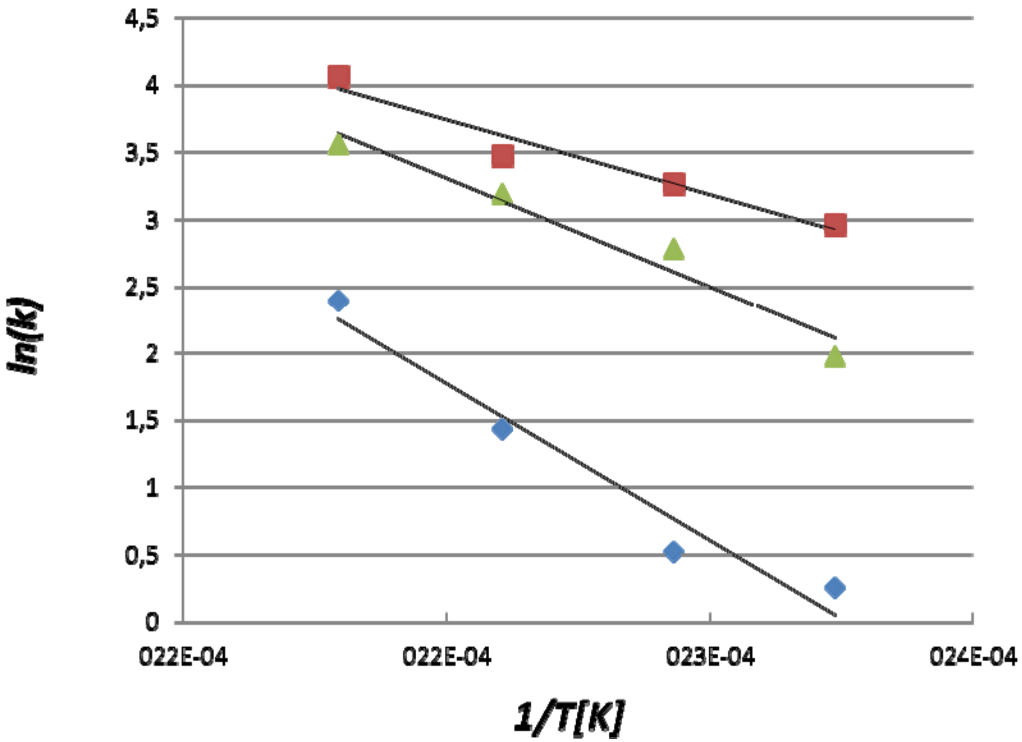


Vulcanization temperatures (°C): 151, 160, 170, 180

Experimental data elaborated through Arrhenius equation

Kinetics of vulcanization

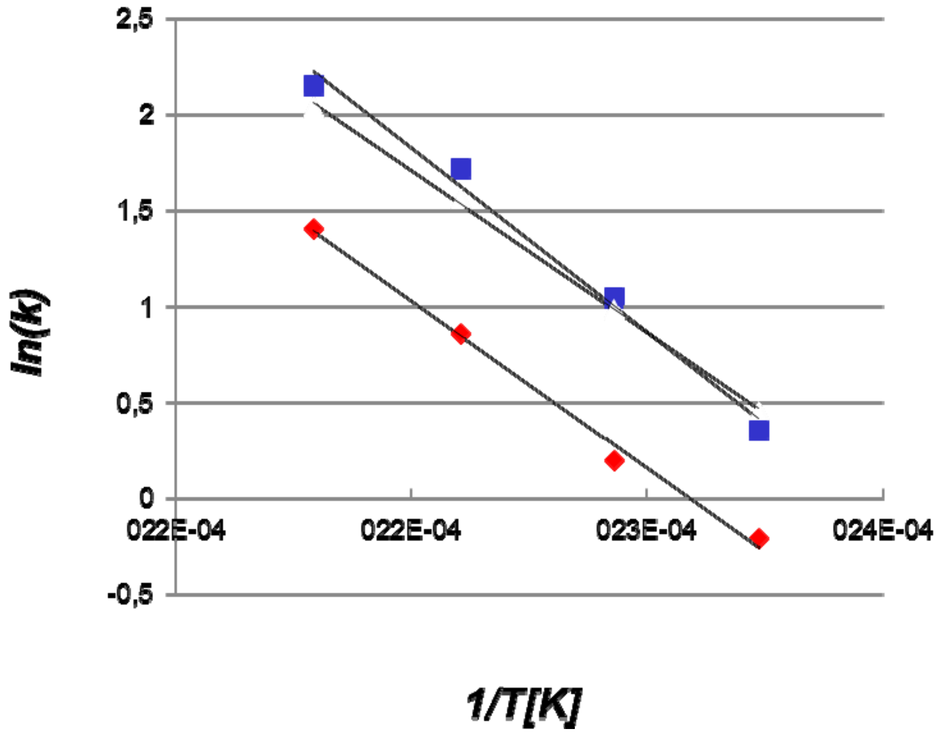
Induction



	Ea (kJ/mol)
Serinol	57.7
SCam	84.7
Ref.	121.2

Kinetics of vulcanization

Crosslinking

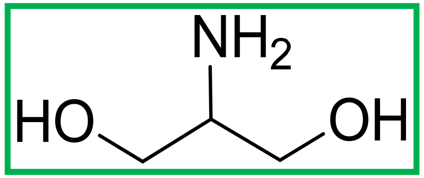


	Ea (kJ/mol)
Serinol	99.7
SCam	84.7
Ref.	91.1

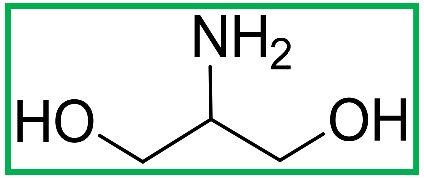
Conclusions

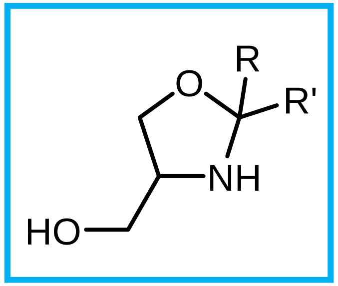
Conclusions

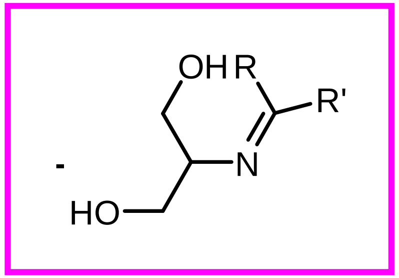
Conclusions



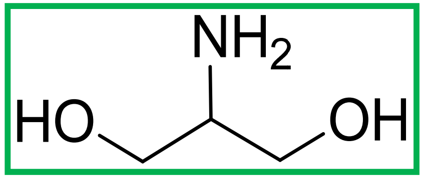
Conclusions

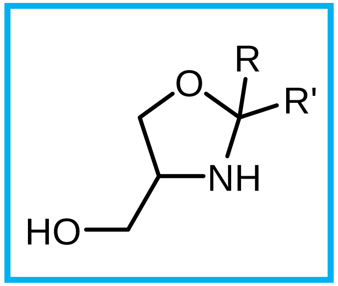


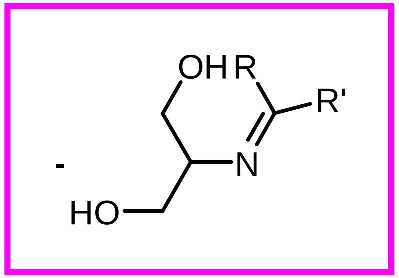


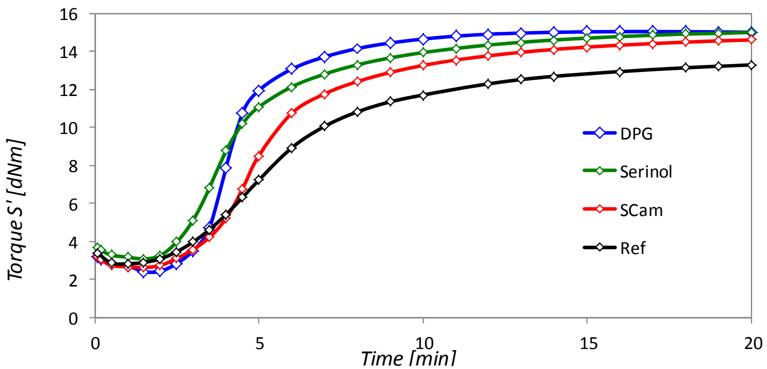


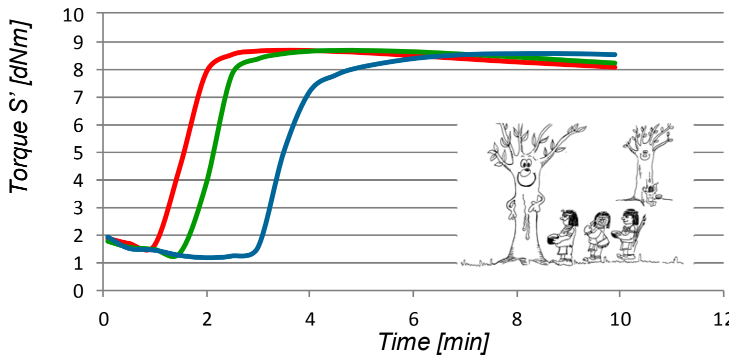
Conclusions











Acknowledgments

- ☞ BUCT (Beijing) for supporting Shuquan Sun PhD period at Politecnico

- ☞ Pirelli Tyre

Rubber Division
American Chemical Society

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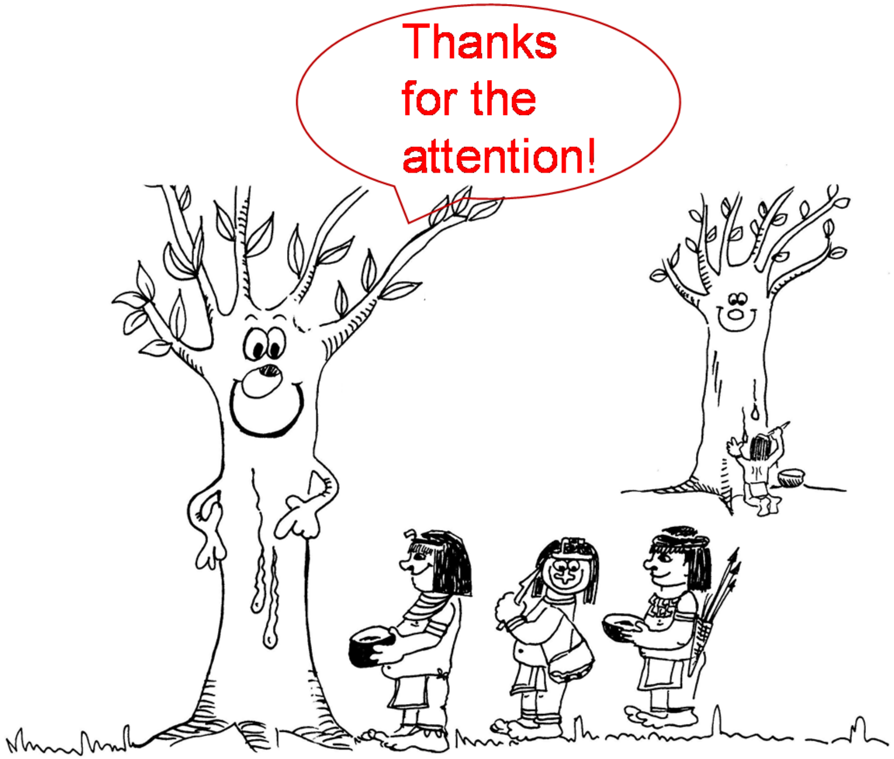
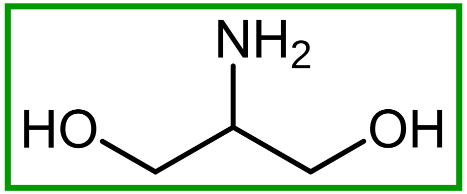
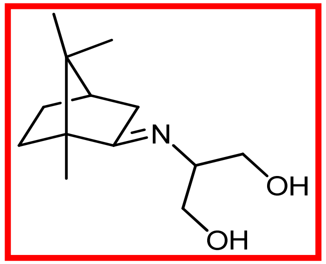

Thanks
for the
attention!

ISCaMaP

Innovative Sustainable Chemistry and Materials and Proteomics Group





Hydrolysis of serinol imines

Mechanism