Sustainable materials for tyres. 3.
Biobased secondary accelerators for silica based compounds

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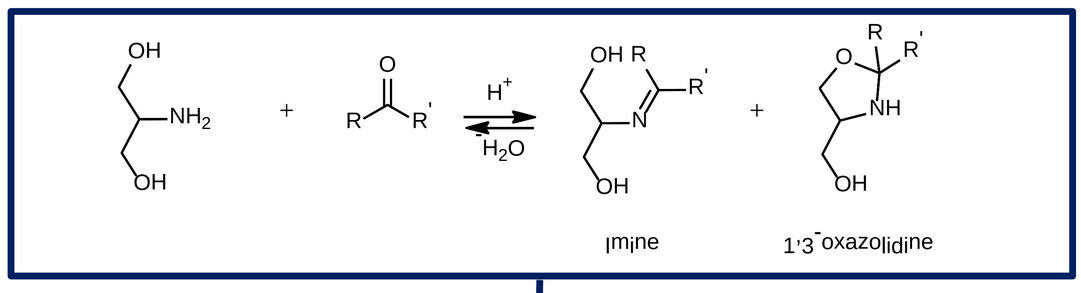
Objectives

- High-yield regioselective synthesis of imines and 1,3-oxazolidines from the biobased starting building block 2-amino-1,3-propanediol (serinol) and aldehydes or ketones, in the absence of solvents acid catalysts
- Use of the resulting imines and 1,3-oxazolidines as accelerators and in the vulcanization of silica based elastomeric composites
- Replacement of diphenylguanidine or petroleum-based chemicals with serinol and its derivative, in order to minimize the environmental impact

Results and discussion

Synthesis of a mixture of imine and 1,3-oxazolidine by condensation of serinol and carbonyl compounds:

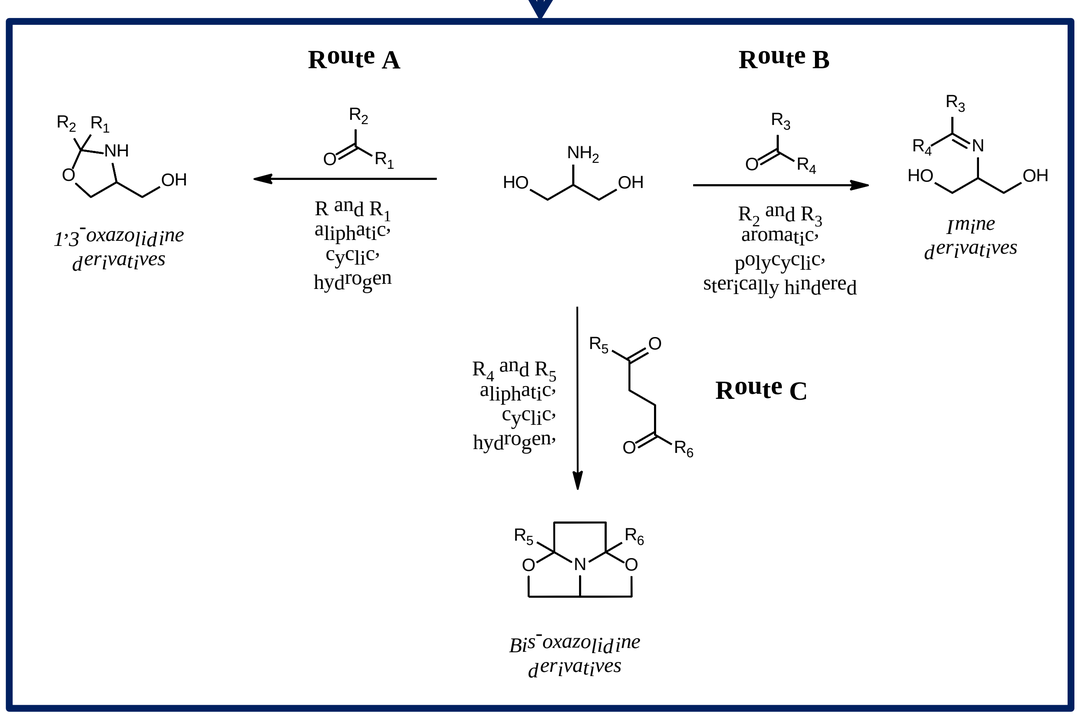
The reaction is usually performed by using acid catalysts in the presence of solvents such as benzene or toluene



Problems:

- Mixtures of imine and 1,3-oxazolidine
- Ring-chain tautomerism

Synthetic routes to 1,3-oxazolidines (Routes A and C), imines (Route B), from the reaction of serinol with carbonyl compounds



Aim of this work is the selective neat synthesis of imines and 1,3-oxazolidines:

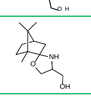
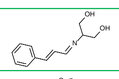
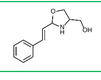
- green conditions
- no acid catalyst
- no solvent

Products characterized by: ^{1}H-NMR, ^{13}C-NMR, GC/MS, IR, Mass spectrometry

Molecular Modelling

Density functional theory (DFT) methods have been employed in order to support the rationalization of the experimental results. The analysis of the results clearly shows that the thermodynamically more stable structures are formed

Table 1. Relative electronic energies (Erel), enthalpies (Hrel, at 298K) and free energies (Grel, at 298K) of selected molecular systems as obtained at the DFT-D (B3LYP/6-31G**) level

Compound	E_{rel} kcal/mol	H_{rel} kcal/mol	G_{rel} kcal/mol
	0.00	0	0
	8.61	7.67	4.12
	8.72	7.86	5.43
	0.00	0	0
	0.00	0	0
	13.04	12.14	9.37
	0.00	0	0
	1.29	2.19	2.89

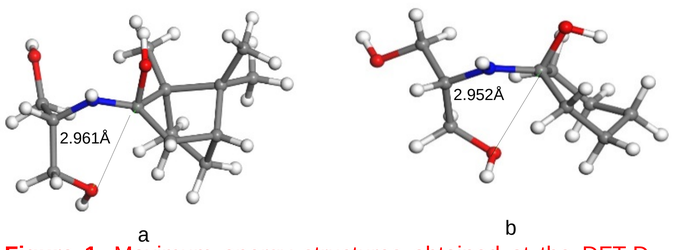


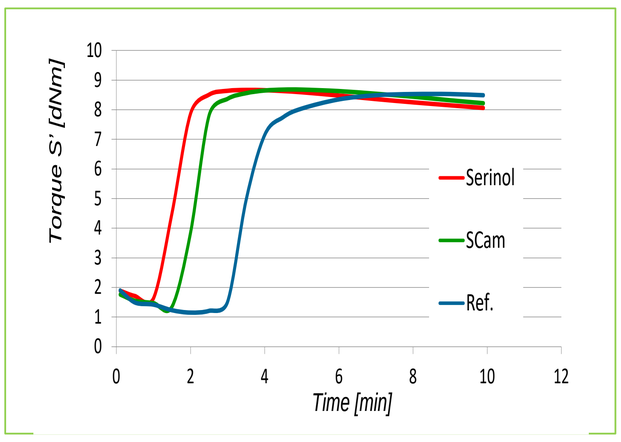
Figure 1. Maximum energy structures obtained at the DFT-D (B3LYP/6-31G**) level. a: intermediate coming from serinol and camphor; b: intermediate coming from serinol and ciclohexanone

Crosslinking of natural rubber

Table 2. Natural rubber (NR) based composites. [a]Recipes amounts are in parts per hundred rubber (phr); [b]CBS: *N*-cyclohexyl-2-benzothiazole sulfenamide; [c]S: serinol; [d]SCam: imine of serinol with camphor

Ingredient	Composite		
	1	2	3
NR	100.0	100.0	100.0
Stearic acid	2.0	2.0	2.0
ZnO	5.0	5.0	5.0
Sulphur	2.0	2.0	2.0
CBS[b]	1.5	1.5	1.5
S[c]	0.0	**0.83**	0.0
SCam[d]	0.0	0.0	**2.04**

Figure 2. Rheometric curves for the crosslinking reaction performed at 151°C of composites of Table 2



Parameter	Measure unit	Composite		
		1 Reference (Ref)	2 Serinol 	3 Scam 
M_L	[dNm]	1.2	1.6	1.3
M_H	[dNm]	8.5	8.7	8.7
t_{s1}	[min]	3.2	1.1	1.8
t_{90}	[min]	4.6	2.0	2.6

Table 3. Parameters of crosslinking of NR based composites

M_L: minimum modulus; M_H: maximum modulus; t_{s1}: time required to have a torque equal to M_L+1; t_{90}: time required to achieve 90% of the maximum modulus M_H

Conclusions

The synthetic routes of either imines or 1,3-oxazolidines from serinol and carbonyl compounds are here reported. Such regioselective reactions allowed the synthesis of families of chemicals, which can find innovative applications as efficient accelerators in natural rubber crosslinking, replacing harmful oil based organic molecules

References:

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2. V. Barbera, S. Musto, G. Infortuna, V. Cipolletti, A. Citterio, S. Sun, M. Galimberti, "Serinol derivatives for the sustainable vulcanization of diene elastomers" accepted for publication on Rubber Chemistry and Technology Frontiers Edition Rubber Chemistry and Technology: 2018, Vol. 91, No. 4, pp. 701-718.
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Acknowledgement: Thanks to Prof. Antonino Famulari for DFT calculation and Pirelli Tyre for the financial support