# Environmentally friendly and regioselective one-pot synthesis of imines and oxazolidines serinol derivatives and their use for natural rubber crosslinking


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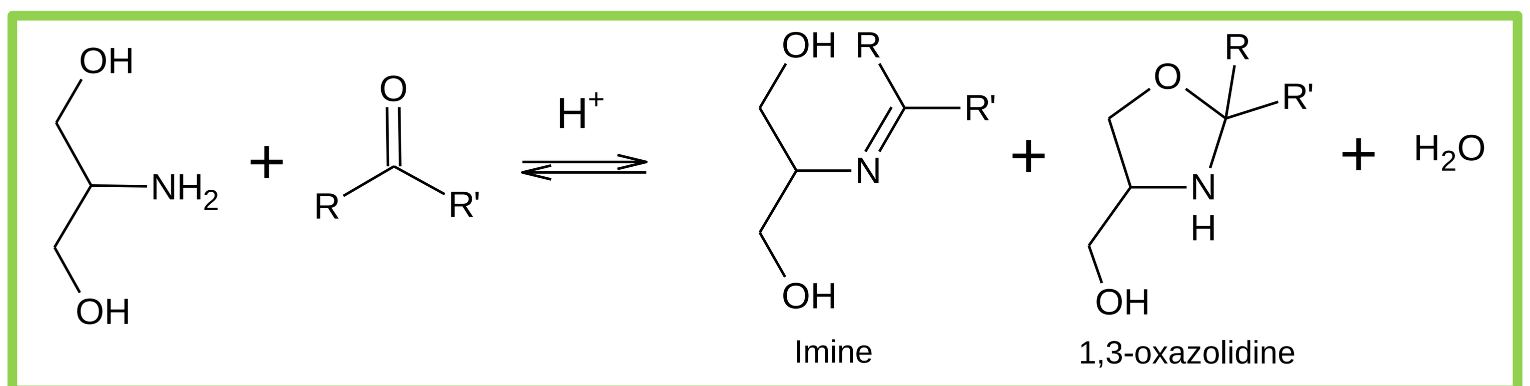
## Objectives

- High-yield regioselective synthesis of imines and 1,3-oxazolidines from the biobased starting building block 2-amino-1,3-propanediol (serinol) and aldehydes and ketones, in the absence of solvents and acid catalysts
- Use of the resulting imines and 1,3-oxazolidines as accelerators in the vulcanization of silica based elastomeric composites

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

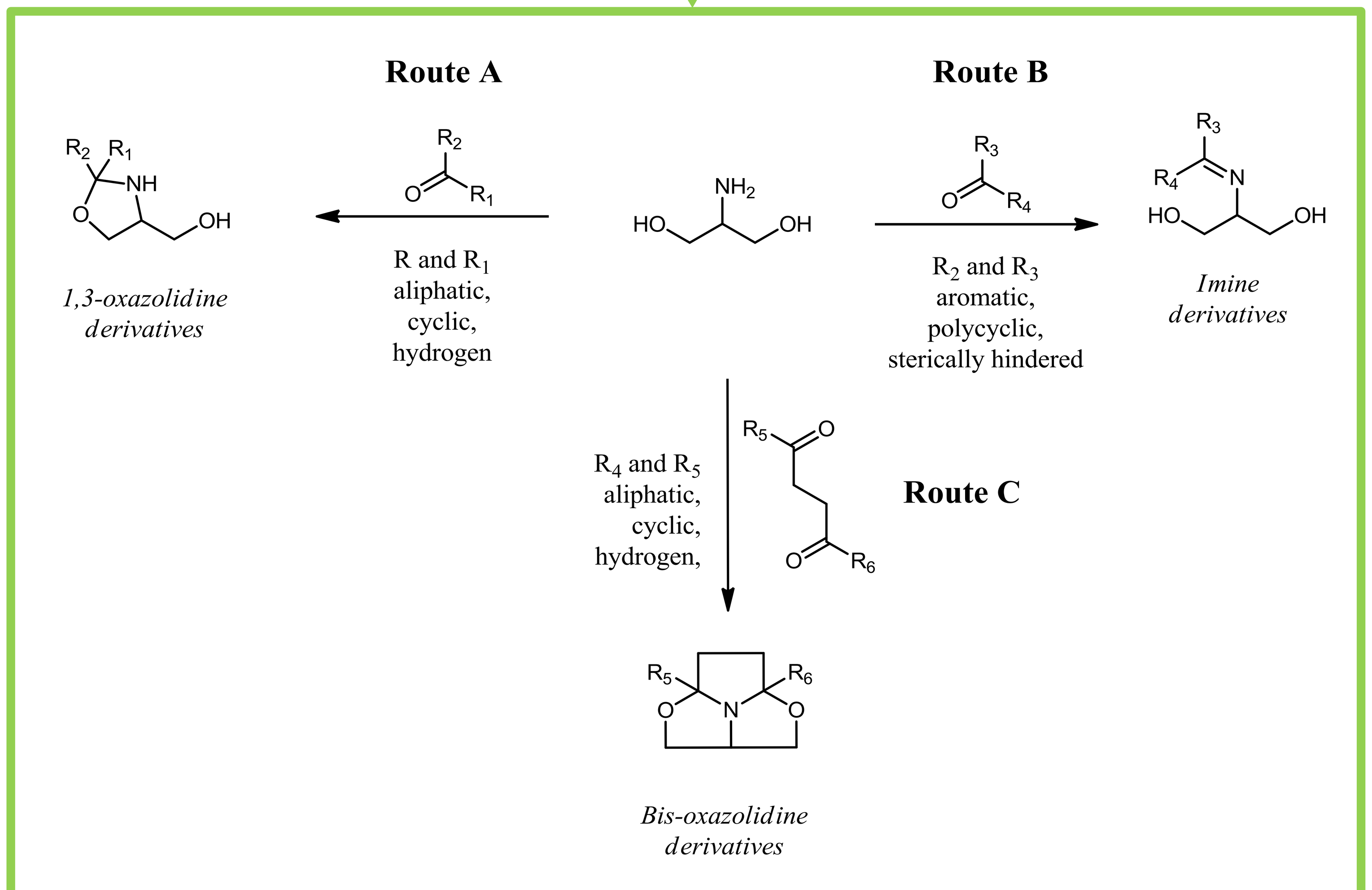



This usually used procedure involves the use of acid catalyst in the presence of solvents such as benzene or toluene

- Presence of mixtures
- Ring-chain tautomerism

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

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




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

- green conditions
- no acid catalyst
- no solvent

## Molecular Modelling

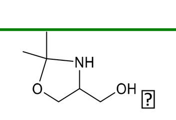
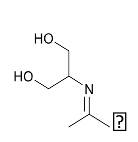
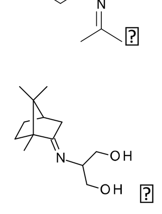
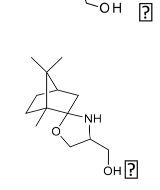
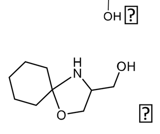
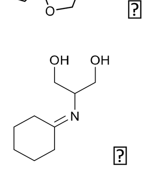
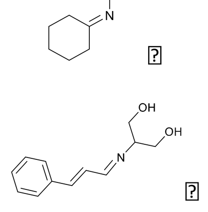
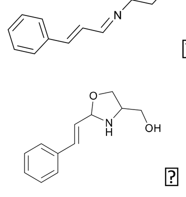
| Compound | $E_{rel}$ kcal/mol | $H_{rel}$ kcal/mol | $G_{rel}$ kcal/mol |
|---|---|---|---|
|  | 0.00 | 0 | 0 |
|  | 8.61 | 7.67 | 4.12 |
|  | 8.72 | 7.86 | 5.43 |
|  | 0.00 | 0 | 0 |
|  | 0.00 | 0 | 0 |
|  | 13.04 | 12.14 | 9.37 |
|  | 0.00 | 0 | 0 |
|  | 1.29 | 2.19 | 2.89 |

**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**

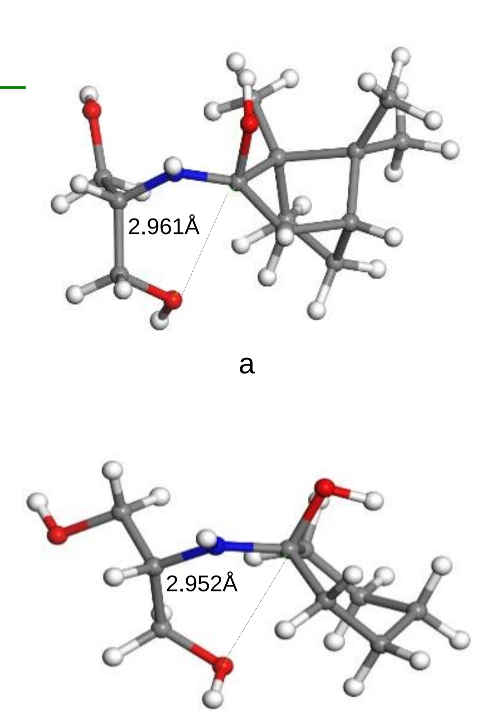



**Figure 1. Maximum energy structures obtained at the DFT-D (B3LYP/6-31G**) level. a: intermediate coming from serinol and camphor; b: intermediate coming from serinol and ciclohexanone**

## Crosslinking of natural rubber

| 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 | 1.5 | 1.5 | 1.5 |
| S[b] | 0.0 | 0.83 | 0.0 |
| SCam[c] | 0.0 | 0.0 | 2.04 |

**Table 2. NR based composites recipes[a]**
**[a]amounts are in parts per hundred rubber (phr)**
**[b]S: serinol; [c]SCam: imine of serinol with camphor**
**1: Ref; 2: serinol; 3: scam**

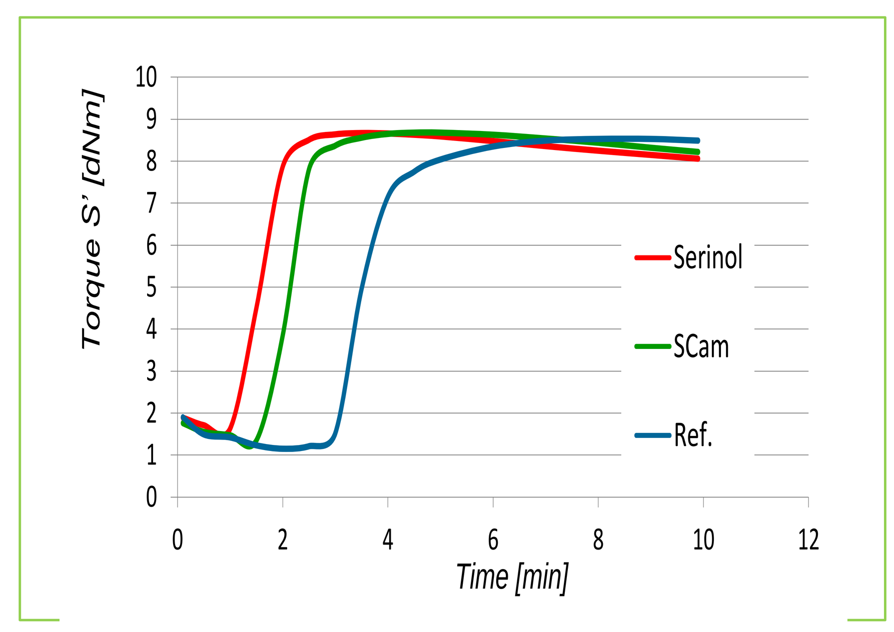



**Figure 2. Rheometric curves for the crosslinking reaction performed at 151°C of composites of Table 2**

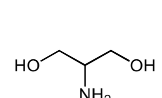
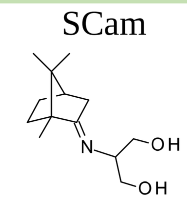
| Parameter | Measure unit | Composite | | |
|---|---|---|---|---|
| | | Ref (Ref) | Serinol  | SCam  |
| $M_L$ | [dNm] | 1.2 | 1.6 | 1.3 |
| $M_H$ | [dNm] | 8.5 | 8.7 | 8.7 |
| $t_{s1}$ | [min] | 3.2 | 1.1 | 1.8 |
| $t_{90}$ | [min] | 4.6 | 2.0 | 2.6 |

**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:**


[1] Bergmann, E. D. (1953). The Oxazolidines. Chemical Reviews, 53(2), 309-352;
[2] Astudillo, M. E. A., Chokotho, N. C., Jarvis, T. C., Johnson, C. D., Lewis, C. C., & McDonnell, P. D. (1985). Hydroxy Schiff base-oxazolidine tautomerism: apparent breakdown of Baldwin's rules. Tetrahedron, 41(24), 5919-5928;
[3] Coran, A. Y. (2005). Vulcanization. In Science and Technology of Rubber (Third Edition) (pp. 321-366)



**Acknowledgement:** Pirelli Tyre is acknowledged for the financial support