

A new chemistry of 2-oxazolines derivatives.

Murilo B. M. de Mello (PG)¹, Leandro Piovan (PQ)¹, Giuliano C. Clososki (PQ)² and Alfredo R. M. de Oliveria (PQ)^{1*}

¹ Universidade Federal do Paraná – Departamento de Química – Centro Politécnico – Curitiba –PR

² Faculdade de Ciências Farmacêuticas de Ribeirão Preto, Universidade de São Paulo – Ribeirão Preto - SP.

Keywords: differentially substituted 2-oxazolines; 2-oxazoliny chalcogen ethers; chiral 2-oxazolines.

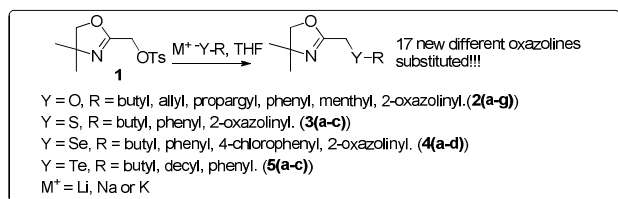
Introduction

The anion derived from 2-methyl-2-oxazoline is the most frequently explored species in chemistry of 2-oxazolines. It has been employed in the synthesis of carboxylic acid homologues,¹ lactones and organometallic reagents, among others.² A clever way to use 2-methyl-2-oxazolines is by placing a leaving group at the 2-position like in 2-chloromethylene-2-oxazolines, well described by Langlois and Florio.³ However, due to environmental restrictions such the use of carbon tetrachloride in the chlorination step, which is usually made by *t*-butylhypochloride.

Herein, we wish to report the development of an alternative building block to be used in place of 2-chloromethylene-4,4-dimethyl-2-oxazoline.

Results and Discussion

We initiate our studies by investigating the application of tosylate **1** in the synthesis of 2-oxazoliny chalcogenides (Scheme 1). Hence compounds **2(a-g)** were obtained in 70 to 90% yield. To extend the method, several 2-oxazolines bearing a chalcogen placed at the 2 position was obtained (compounds **3, 4** and **5**).



Scheme 1. General route for the synthesis of 2-oxazolines chalcogenide substituted.

Interestingly, the telluride **5a** was highly sensitive to light and oxygen. It could only be isolated by using a helium gas atmosphere during the flash chromatography in a dark chamber. The decomposition of **5a** was monitored by ¹²⁵Te NMR and after 45 minutes exposed to air, ambient light and at room temperature, it was not possible to observe any tellurium containing material (See Figure 1). The consumption of telluride **5a** was followed by the precipitation of a white solid insoluble in several organic solvent systems.

It is known that when aryl benzyl tellurides are submitted to a similar oxidative process⁴, only their benzyl portion is oxidized and no aryl oxidation

38ª Reunião Anual da Sociedade Brasileira de Química

product is detected.⁵ This characteristic prompted us to synthesize the compounds **5b** and **5c**, with 60% and 68% yield.

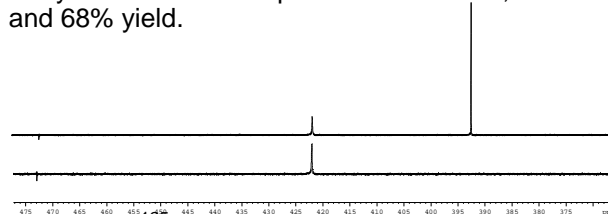
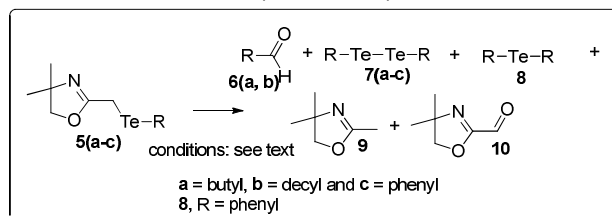


Figure 1. ¹²⁵Te NMR (CDCl₃) spectrum showing the disappearing **5c** signal at 393 ppm. (Ref. PhTeTePh at 422 ppm).

When **5b** was submitted to cold white light under O₂ atmosphere, compounds **6b, 7b, 9, 10** and 1-decene was detected by GC-MS. When compound **5c** was irradiated in same conditions, no β-elimination product was detected and only compounds **7c, 8, 9** and **10** were formed. (Scheme 2)



Scheme 2. Degradation of 2-oxazoliny tellurides.

Conclusion

Tosylate **1** is an important moiety in 2-oxazolines allowing the synthesis of several new derivatives. The telluro-oxazolines **5(a-c)** were unstable and from its decomposition the aldehyde **10** was isolated and characterized.

Acknowledgements

CAPES, CNPq, Fundação Araucária e UFPR

1 T. G. Gant, A. I. Meyers, *Tetrahedron Rep.* **1994**, 50, 2297.

2 G. Desimoni, G. Faita, K. A. Jørgensen, *Chem. Rev.*, **2011**, 284;

3 Florio, S., *Synlett*, **2013**, 24, 1061.

4 H. K. Spencer, M. P. Cava, *J. Org. Chem.*, **1977**, 42, 2937;

5 J. T. B. Ferreira, A. R. M. Oliveira, J. V. Comasseto, *Tetrahedron Lett.* **1992**, 33, 915