

Synthesis of Substituted Benzoxazolinones by the Curtius Rearrangement: Crystal Structures of Intermediates and By-Products

Gerhard Laus^a, Volker Kahlenberg^b, Klaus Wurst^a, Sven Nerdinger^c,
and Herwig Schottenberger^a

^a Faculty of Chemistry and Pharmacy, University of Innsbruck, 6020 Innsbruck, Austria

^b Institute of Mineralogy and Petrography, University of Innsbruck, 6020 Innsbruck, Austria

^c Sandoz GmbH, 6250 Kundl, Austria

Reprint requests to Prof. Dr. Herwig Schottenberger. Fax: (+43) 512 507 2934.

E-mail: herwig.schottenberger@uibk.ac.at

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3-Substituted salicyloyl chlorides were converted to salicyloyl azides (R = Br, NO₂) which underwent thermal rearrangement and intramolecular cyclization to benzoxazolinones. The crystal structures of 7-substituted benz[*d*]oxazolin-2-ones (R = Br, NH₂), intermediate salicyloyl azides and by-products, *i. e.* 3-(2-hydroxy-3-nitrophenyl)-8-nitrobenz[*e*][1,3]oxazine-2,4-dione and 2-hydroxy-*N*-(2-hydroxy-3-nitrophenyl)-3-nitrobenzamide, have been determined. 7-Aminobenzoxazolinone was obtained by catalytic hydrogenation of the nitro compound as the hemihydrate or in anhydrous form, depending on the temperature of the crystallization.

Key words: Acyl Azide, Benzoxazolinone, Crystal Structure, Curtius Rearrangement