Rearrangements of N-Aryl Hydroxamic Acid Methanesulfonates: Towards Novel and Valuable Organic Substances

Martinkova, Veronika (School: Gymnazium Frantiska Palackeho Valasske Mezirici)

N-Aryl hydroxamic acids (NAHAs) represent a group of valuable synthetic intermediates. Their N OH modification, by appending good leaving group (LG), triggers intramolecular rearrangement leading to the N-O bond cleavage and migration of the O-LG moiety into the aromatic ring. The developed reaction sequence is straightforward and affords variety of new organic molecules, otherwise inaccessible. Perspective applications of these novel organic substance is seen as valuable starting materials for organic synthesis, pharmacochemistry, biochemistry, materials chemistry, catalysis, drugs, polymers, etc. Chemo- and regioselectivity of the NAHA rearrangement were examined in relation to the appended electron-withdrawing/donating substituents in order to explore the basic reactivity pattern and to elucidate structure-property relationships. Upon treating the NAHA derivatives with methanesulfonyl chloride, the rearrangement took place spontaneously. NAHA derivatives with OMe or NHAc substituents reacted faster than those bearing electron-withdrawing groups. It turned out that the reaction proceeds via ionic transition state, which allows OMs - Cl exchange and resulted in chlorination of aromatic ring. The migration to the position 2 of 4-substituted derivatives ruled out alternative mechanism via [3,3]-sigmatropic rearrangement. In overall, thirty derivatives were synthesized, of which fourteen are completely new organic substances. All target products and their structure and purity were thoroughly determined by various analytical methods including HPLC/MS and NMR.

Awards Won: